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TREATMENT OF FERROUS ACID MINE DRAINAGE WITH ACTIVATED CARBON

Charles T. Ford, et al

Bituminous Coal Research, Incorporated
Pittsburgh, Pennsylvania

January 1973

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Treatment of Ferrous Acid Mine Drainage with Activated Carbon

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An evaluation of this process indicated technical feasibility which would permit acid mine drainage neutralization using an inexpensive reagent, such as limestone. The major disadvantage is the cost of the activated carbons since they are rendered inactive after relatively short use by apparently irreversible adsorption of iron. This cost appears to be sufficiently high to prohibit the use of this process for treating coal mine drainage. ~~(Ford-Bituminous Coal Research, Inc.)~~ (EPA)

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TREATMENT OF FERROUS ACID MINE DRAINAGE WITH ACTIVATED CARBON

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ABSTRACT

Laboratory studies were conducted with activated carbon as a catalyst for oxidation of ferrous iron in coal mine water. Batch tests and continuous flow tests were conducted to delineate the process variables influencing the catalytic oxidation and to determine the number and types of coal mine water to which this process may be successfully applied.

The following variables influence the removal of iron with activated carbon: (a) amount and particle size of the carbon; (b) pH, flow rate, concentration of iron, temperature, and total ionic strength of the water; and (c) aeration rate. Adsorption as well as oxidation are the mechanisms involved in iron removal by this process.

An evaluation of this process indicated technical feasibility which would permit acid mine drainage neutralization using an inexpensive reagent, such as limestone. The major disadvantage is the cost of the activated carbons since they are rendered inactive after relatively short use by apparently irreversible adsorption of iron. This cost appears to be sufficiently high to prohibit the use of this process for treating coal mine drainage.

This report was submitted by Bituminous Coal Research, Incorporated in fulfillment of Project Number 14010GYH under the joint sponsorship of the Environmental Protection Agency and Bituminous Coal Research, Incorporated.

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SECTION I

CONCLUSIONS

Studies on the treatment of ferrous acid mine drainage with activated carbon have led to the following conclusions:

1. A process has been developed whereby ferrous iron can be removed from acid mine drainage at low pH with activated carbon. The use of this process can result in almost complete removal of the ferrous iron.

2. The process essentially consists of streaming the acid mine drainage through an aerated column containing a bituminous coal-based activated carbon. The effectiveness of removal of ferrous iron is dependent on the amount of carbon used, the water flow rate, and the concentration of iron in the water.

3. The advantage of this process is that once the ferrous iron has been removed, the acid mine drainage can be more readily neutralized using an inexpensive reagent such as limestone.

4. The major disadvantage of the process is that the activated carbon soon loses its activity by adsorption of the iron on the carbon. This adsorbed iron cannot readily be removed, for example by an acid wash, and the relatively expensive activated carbon must be discarded. Costs for activated carbon alone might range from $62 to $165 for every 1,000 gallons of water treated. The cost would prohibit this process for use in treating acid mine drainage.

5. The process is limited to waters having a pH below 4.0 but higher than 2.5. Above pH 4.0, the precipitated iron compounds would physically clog the column; below pH 2.5, the use of carbon results in a significant reduction of iron back from the ferric to the ferrous state, which is the opposite reaction desirable to this process.

6. Of relatively minor importance are the effects on ferrous iron removal of particle size of the carbon, temperature and total ionic strength of the water, and aeration rate. The surface area of the carbon and the concentrations of aluminum, manganese, and sulfate in the water had no effect on iron removal.

SECTION II

RECOMMENDATIONS

The following additional studies are recommended:

1. Larger scale continuous flow tests with activated carbon, including neutralization, should be conducted with acid mine drainage to determine if a lesser degree of iron removal than that used in the process evaluation would be sufficient to initiate iron removal. Adequate treatment might still be obtained since treatment with limestone involves additional iron removal as well as neutralization. For this purpose, treatment at a water flow rate of at least one gallon per minute is recommended.

2. Examination should be made of an inexpensive method for removing the adsorbed iron from the activated carbon.

3. Additional tests should be conducted with other materials, such as coal, instead of activated carbon, and with the use of oxygen rather than air.

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SECTION III

INTRODUCTION

This is the final and summary report on the Environmental Protection Agency (EPA) Project No. 14010 GYH activated June 1, 1971, with financial support from Bituminous Coal Research, Inc., and the Environmental Protection Agency. The project is based in part on exploratory work conducted on Pennsylvania Coal Research Board Project CR-75, activated July 1, 1967, with financial support from Bituminous Coal Research, Inc., the Pennsylvania Coal Research Board, and the United Mine Workers of America, and expanded February 7, 1968 with additional financial support for the program through Grant WPRD 63-01-68 to the Commonwealth of Pennsylvania by the Federal Water Pollution Control Administration.(1)

Work on the project was conducted according to the BCR Research Program Proposal RPP-171R, dated November 19, 1970, and the Grant Application, dated May 18, 1971, both of which were submitted to the Environmental Protection Agency. A schedule of work detailing the plan of operation used on the project was also submitted to EPA on July 7, 1971. The experimental work was conducted during the period June 1, 1971 to May 31, 1972.

Objectives

The objectives of the studies conducted in the period covered by this report were to delineate the process variables influencing the catalytic oxidation of ferrous iron with activated carbon and to determine the number and types of coal mine water to which this process may be successfully applied.

This work is a part of a long-range program being conducted at BCR the objective of which is to design and develop an improved process, based on treatment with limestone, for the control and prevention of pollution of waters by drainage from coal mines.

Nature and Scope of the Problem

The occurrence of acid drainage associated with coal mining has been well documented.(2) By 1970, over 200 mine water treatment plants were operating and an additional 100 plants were in various stages of design and construction in the state of Pennsylvania alone as part of the coal industry's vigorous abatement program of constructing water treatment plants wherever polluting waters might be discharged from active mines into open streams.(3)

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Because of certain conditions, treatment of coal mine water by neutralization does not always proceed as rapidly as desired. Specifically, treatment of coal mine water containing iron in the ferrous, Fe^{2+}, state involves oxidation as well as neutralization, and this oxidation is responsible for generating more acid. The oxidation and hydrolysis of each mole of ferrous iron, Fe^{2+}, results in a net gain of two moles of acid, H^+, to the system as can be seen in the following equations:

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O$$

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3H^+$$

The oxidation and hydrolysis of the resultant product of oxidation to a more insoluble ferric compound, the familiar yellowboy, is responsible for slowing up the treatment process since the acid produced requires further neutralization. The problem is particularly acute when limestone is the neutralizing agent (4) since limestone is comparatively insoluble and a weakly basic material. In a continuous limestone treatment process, the pH rarely increases to as high as 7. Since the rate of oxidation of ferrous iron increases a hundredfold for every increasing unit of pH (5, 6), that rate cannot be accelerated by pH control with limestone, as is possible during treatment with lime, soda ash, or sodium hydroxide. In addition, other processes which might be used for treatment of coal mine water, e.g., reverse osmosis (7), have exhibited problems associated with the oxidation of ferrous iron.

The present program of laboratory investigation was designed to aid in solving these problems.

Approach to the Problem and Research Procedure

The approach taken to oxidation of ferrous iron in coal mine water with activated carbon was conceived, for the most part, as a result of two publications. The first, a 1944 patent by Schumacher and Heise (8), described the preparation and use of activated carbons to oxidize "aqueous solutions of salts of metals of variable valency." The second, a 1965 publication by Thomas and Ingraham (9), described studies of the rate of oxidation of aqueous ferrous sulfate solutions using activated carbon as a catalyst. Both were concerned with catalytic oxidation of leach liquors which routinely consisted of concentrated amounts of iron in contrast to the more dilute concentrations of iron typically found in coal mine drainage.

As early as 1931, the concept had been tested by Lamb and Elder (10) using a commercial, steam-activated, coconut charcoal and later in 1953 by Posner (11) using a catalyst prepared from sugar, $FeCl_3$, and urea. The concept was tested at BCR in 1967 (12) and found to be feasible as part of the limestone treatment research program (1, 13) and later under a separate research program, BCR Project No. 2040. Early in 1968, as part of the limestone treatment program (1), the procedure of preparing activated carbons for testing was abandoned and commercially available materials were obtained and tested (14, 15) with favorable results. The Bureau of Mines, in a limited study (16) conducted in 1969 in cooperation with the Pittsburgh Activated Carbon Division of Calgon Corporation, confirmed our earlier results.

To delineate the process variables influencing the catalytic oxidation of ferrous iron with activated carbon and thereby achieve one of the stated objectives of this program, both batch and continuous flow experiments were conducted. The first part of the program involved the use of laboratory-prepared synthetic coal mine waters. The latter portion of the program involved actual coal mine waters to aid in achieving the other stated objective of the program which was to determine the number and types of coal mine waters to which this process might be successfully applied.

Consideration was given early in this project to statistical design (17, 18, 19) and, more specifically, to sequential analysis (20, 21, 22, 23), and these techniques were used where appropriate to obtain the maximum amount of useful information from the experimentation.

Process variables explored during this study included (a) the surface area, particle size, and origin of the activated carbons; (b) the pH and concentrations of iron, aluminum, manganese, and sulfate as well as the temperature of the mine water; (c) the aeration rate and flow rate of water through the carbon columns; and (d) the configuration of the carbon column. The role of bacteria in this process was examined by (a) analyzing the waters for bacteria which might influence the process and (b) inoculating some waters or carbons with Thiobacillus ferrooxidans and/or Thiobacillus thiooxidans.

Procedures used, process variables explored, and conduct of the experiments on this project were selected by mutual agreement between BCR personnel and the sponsors (EPA) prior to and during the experimental program.

SECTION IV

EXPERIMENTAL

General procedures, including apparatus, materials, and analytical procedures for conducting the experiments and for evaluating the effect of process variables, are reported here.

Analytical Procedures

Both raw mine water and treated water samples were analyzed routinely for pH and for ferrous and total iron colorimetrically (24) using o-phenanthroline and a Hach Chemical Co. Model AC-DR colorimeter. Iron, aluminum, and manganese were determined by emission spectrographic techniques using a Jarrell Ash Model 78-000 1.5 meter Wadsworth grating or by atomic absorption techniques using an Instrumentation Laboratory Model IL-153 atomic absorption spectrophotometer. Sulfates were determined gravimetrically. Dissolved oxygen was determined with a Yellow Springs Model 54 oxygen meter equipped with a Clark-type membrane-covered polarographic probe.

General Procedures

The general procedure for conducting the batch experiments was as follows:

A 16 g portion of activated carbon was placed in a gas washing bottle with 150 ml of synthetic coal mine water. Air was bubbled at a rate of 150 ml/min through the carbon-water mixture and the water analyzed at specified periods of time. For most tests, ferrous iron, Fe^{2+}, and total iron, Fe_T, as well as pH were determined. A sketch of the apparatus used for these experiments is shown in Figure 1. The gas washing bottles are a standard, off-the-shelf item (Fisher Scientific, Catalog No. 3-037) consisting of a Pyrex bottle approximately 270 mm overall height, 350 ml capacity with a side inlet and fritted disc 60 mm in diameter at the bottom and a standard taper (S. T. 24/40) ground joint at the top.

The general procedure for conducting the continuous flow experiments was as follows:

A glass column, 19 in. long x 3 in. inside diameter, was packed with 800 g of Nuchar WV-W, 12 x 40 mesh, activated carbon (Westvaco). A rubber stopper and a plastic screen were used to contain the carbon. A reservoir of coal mine water was placed approximately 1.5 ft above the top of the column. The coal mine water flowed through the column at a rate of 30 ml/min. Air, at a rate of 150 ml/min, was introduced by means of a gas dispersion tube inserted down through the activated

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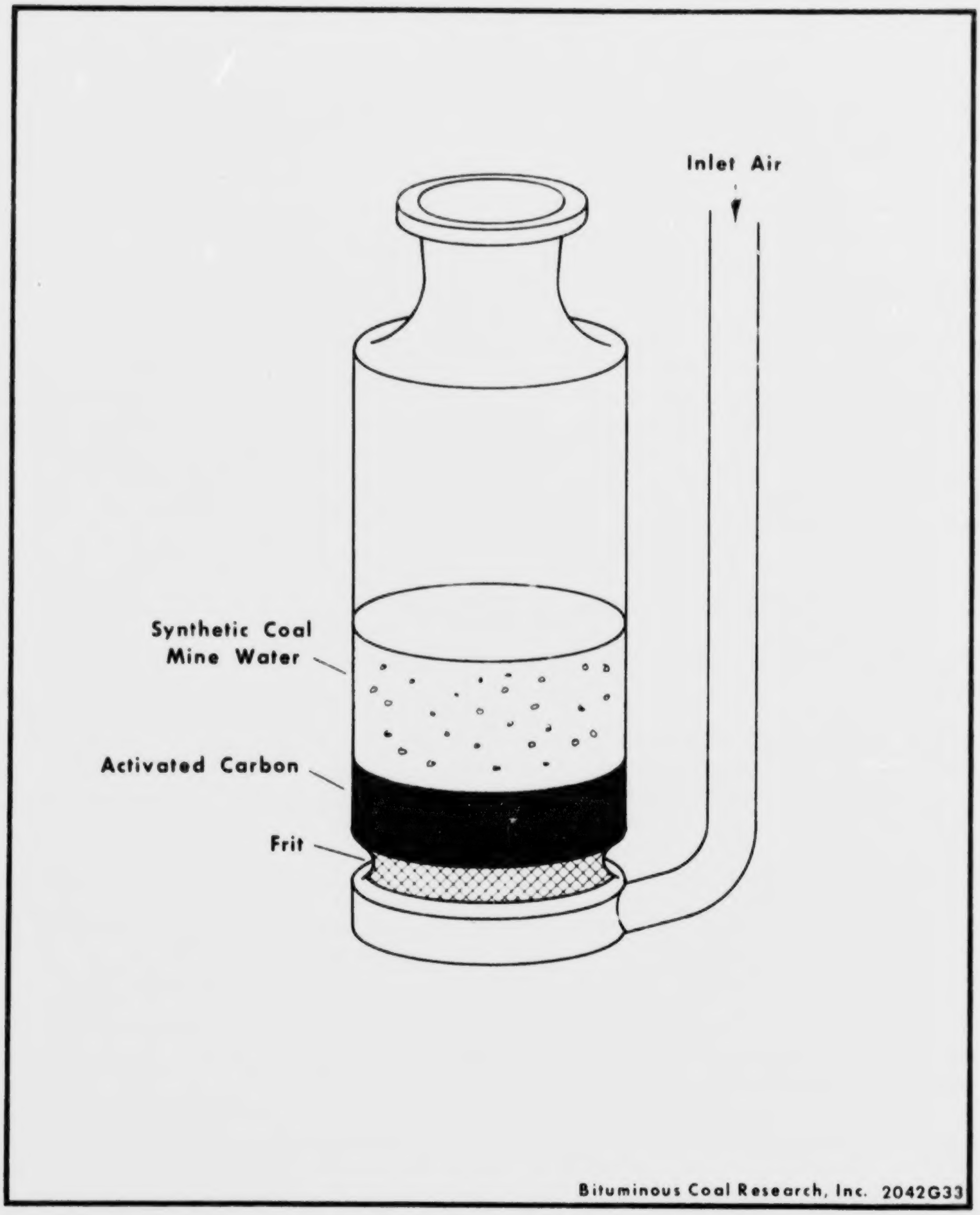
Inlet Air
Synthetic Coal Mine Water
Activated Carbon
Frit
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Figure 1. Apparatus for Batch Experiments on Catalytic Oxidation of Ferrous Iron

carbon to the plastic screen at the bottom of the column. The water was analyzed at specified periods of time, usually for ferrous iron, Fe^{2+}, and total iron, Fe_T, and pH.

A sketch of the apparatus used for most of these continuous flow tests is shown in Figure 2. Preliminary tests were conducted using a similar glass column, 22 in. long x 1 in. inside diameter, packed with 80 g of activated carbon. Tests were also conducted with molded acrylic columns. Other changes in the procedure and apparatus are discussed for the individual tests.

To control the flow of compressed air for the experiments, flowmeter-regulator combinations were mounted on panels. The flowmeters were Dwyer Instruments, Inc., Visi-Float Model VFA-SSV-PF-21. Each was connected to a matching Dwyer Model RKA constant differential pressure regulator behind the panel. The regulators were preset at 3 psi. The flowmeters were calibrated and covered the range of 0.1 to 0.5 liters per minute.

Materials

Activated carbons and corresponding technical information were received from a number of suppliers. Those carbons used in most of the experiments include Westvaco's Nuchar WV-W, 12 x 40 mesh, and Pittsburgh Activated Carbon's Filtrasorb 100 and 300, both 8 x 40 mesh. Other activated carbons will be described as they are used in the experiments.

Synthetic coal mine water was prepared on demand in 15 liter batches. The "standard" synthetic used in most tests consisted of a solution of approximately 250 mg/l of Fe^{2+} added as $FeSO_4 \cdot 7H_2O$ and adjusted to pH 3.0 with sulfuric acid. For other tests, the pH of the synthetic was changed by addition of different amounts of acid to the desired pH. The concentration of iron also was changed in other tests and other constituents such as aluminum, manganese, and sulfate were added to it.

Two actual coal mine waters were used. One was a discharge from an abandoned coal mine in Westmoreland County, Pennsylvania, which contained 13 mg/l of Fe^{2+} and 45 mg/l of Fe_T with a pH of 3.0. The other was a stream sample from a tributary of Little Plum Creek in Allegheny County, Pennsylvania. The concentration of iron varied with the particular spot chosen for sampling. All sampling points of this stream were within 3 miles of each other. The concentration of Fe^{2+} varied from 55 to 390 mg/l, total iron from 71 to 535 mg/l and the pH from 2.8 to 4.6 as the stream was diluted by run-off from various sources.

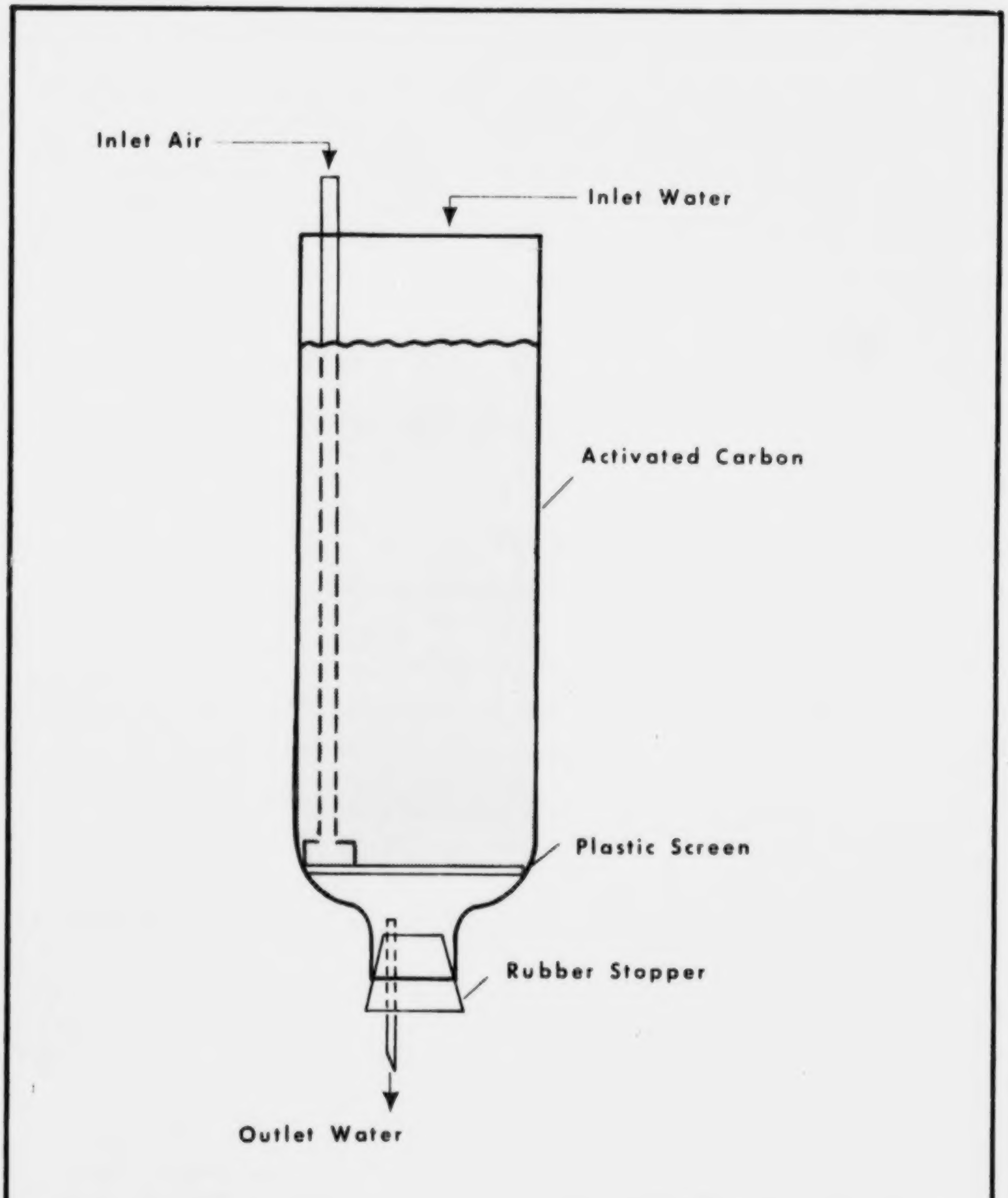

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Figure 2. Apparatus for Continuous Flow Experiments on Catalytic Oxidation of Ferrous Iron

Effect of Variables

Column Design

Preliminary batch and continuous flow tests were conducted to obtain data for design of activated carbon columns for use on this project. Carbons of different particle size and three different glass columns, 22 in. x 1 in., 53.5 in. x 1.5 in., and 19 in. x 3 in. (length x inside diameter) were used in a series of experiments with standard synthetic coal mine water to establish flow rates of the water through the columns. The effects of dry versus wet packing, of omitting aeration or aerating the water exterior to the column, and of aerating by suction on the effectiveness of iron oxidation were determined.

Role of Adsorption

To determine the adsorptive capacity of the carbon, 25 ml aliquots of standard synthetic coal mine water were placed in 500 ml Erlenmeyer flasks with the following amounts of Nuchar WV-W carbon, 12 x 40 mesh: 0.05, 0.10, 0.15, 0.20, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 2.25, 2.50, 5.0, 7.5, 10.0, 12.5, 15.0, 17.5, and 20.0 g. The flasks were each agitated for 60 minutes. At the end of this time, the samples were filtered and analyzed for ferrous iron, total iron, and dissolved oxygen. The experiment was repeated with Nuchar WV-W carbon, minus 325 mesh. In the duplicate experiment with the powdered carbon, only the range 0.05 to 2.00 g of carbon was included.

To determine the oxidation state of the iron adsorbed on the carbon, two 10 g samples of Nuchar WV-W carbon, 12 x 40 mesh, were rinsed with 50 ml of deionized water. One of the samples was placed in 50 ml of standard synthetic coal mine water; the other, which was used as a blank, in deionized water. Each was aerated for 30 minutes, stirred occasionally, and samples taken for Fe^{2+} and Fe_T. Each was removed from the water, rinsed with 50 ml of deionized water (samples taken of the deionized water), removed from the water, extracted with 25 ml of hot (80-90C) 6N HCl, and the acid analyzed for Fe^{2+} and Fe_T.

Batch tests were then conducted according to the general procedure to determine any differences in the rate of adsorption of ferrous iron, Fe^{2+}, and ferric iron, Fe^{3+}, on the surface of the activated carbon. Solutions of 300 ml each of (a) standard synthetic coal mine water and (b) ferric nitrate containing approximately 250 mg/l of Fe^{3+} were added to 32 g portions each of Nuchar WV-W carbon, 12 x 40 mesh, in two 600 ml beakers. The carbon samples had each been soaked overnight in 100 ml of deionized water. Each was stirred at a rate of 51 revolutions per minute (rpm) with identical mixers, and pH, Fe^{2+}, and Fe_T determined at selected intervals for a 24 hour period.

Since no attempt was made to control pH in the previously described batch tests, the tests were repeated and greater pH control was maintained during the repeat tests. Nuchar WV-W carbon, 12 x 40 mesh, 32 g portions for each test, was soaked overnight in 100 ml of deionized water prior to each test. A new portion of carbon was used for each test. The pH of each solution was adjusted to the desired value by adding H_2SO_4 at the beginning of each test. Each solution was then added to the carbon portions which were each in separate 600 ml beakers; the mixture was stirred at a rate of 51 rpm, and pH, Fe^{3+}, and Fe_T were monitored at selected intervals for 300 minutes. Tests were conducted at pH 1.0, 2.0, 2.5, 2.7, 3.0, 4.0, and 5.0.

Results of initial tests showed that the pH of the mixture changed more rapidly if the carbon was agitated slightly; therefore, the mixer was placed into the carbon at the bottom of the beaker. This resulted in gentle agitation of the carbon without aerating the mixture. Results of initial tests also demonstrated that the pH was not maintained at the desired value throughout the test; therefore, the mixture was titrated with H_2SO_4 during the 300-minute test to maintain the desired value throughout the test. A concentration of 3N H_2SO_4 was selected for the titration since the addition of this did not appreciably change the volume of the initial solution and, therefore, change the concentration of iron, yet controlled the pH satisfactorily. It was also discovered in the initial tests that iron precipitated rapidly from the solution of ferric nitrate even at relatively low pH. Fresh solutions were then prepared on the day of the test.

Reduction of Iron

Both batch and continuous flow experiments were conducted with Nuchar WV-W carbon, 12 x 40 mesh, and a synthetic coal mine water containing 250 mg/l of ferric iron, Fe^{3+}, added as $Fe(NO_3)_3 \cdot 9H_2O$. The pH of this water was 2.5. The reduction of iron from the Fe^{3+} state to the Fe^{2+} state in the aerated carbon-water systems was determined by analyzing the water for ferrous and total iron at specified periods of time.

Types of Carbon

Six different carbons having various origins were each used in batch and continuous flow tests. These include, with their origin in parentheses: (a) Barnebey Cheney AE, 4 x 6 mesh (coconut shell); (b) Witco, 4 x 10 mesh (petroleum); (c) Westvaco Nuchar WV-W, 8 x 30 mesh (bituminous coal); (d) Pittsburgh Activated Carbon BPL, 6 x 16 mesh (bituminous coal); (e) Atlas Darco, 4 x 12 mesh (lignite); and Barnebey Cheney 274, 3 x 8 mesh (mineral).

The batch tests were conducted with standard synthetic coal mine water according to the general procedure in the gas washing bottles. The carbon-water mixture was aerated at a rate of 150 ml/min for 120 minutes. Duplicate tests were conducted with the carbon being rinsed with 50 ml of deionized water between tests.

For the continuous flow tests, the general procedure was followed but 400 g each of the same six carbons as were employed in the batch tests were used. Sufficient quantities of Witco carbon, 4 x 10 mesh, and Atlas Darco carbon, 4 x 12 mesh, were not available; therefore, a 4 x 16 mesh and a 4 x 40 mesh fraction, respectively, were used. Synthetic coal mine water flow rate was maintained at 30 ml/min for the first 120 minutes of each test; at 200 ml/min for an additional 30 minutes; and then at 1600 ml/min until the water sample was exhausted. In some cases, 1600 ml/min could not be attained due to the nature of the particular carbon; flow was then set at the maximum attainable.

Statistical Design I

This phase of the research program involved a study of the effects of particle size and surface area of the activated carbon, as well as aeration rate and concentration of ferrous iron in the synthetic coal mine water on removal of iron. To this end, a 2^4 factorial experiment was designed to include these variables. The methodology involved in this factorial experiment was based on a recent publication (18) on statistically designed experiments. The 16 tests required that two carbons be available of the same type or origin with different surface areas and which could be pulverized to different particle size fractions. The carbons selected were Filtrasorb 100 and Filtrasorb 300 (Calgon Corp.)

From the results of preliminary tests, 3 ml of 3N H_2SO_4 was selected as the approximate amount necessary to neutralize 16 g of carbon in 150 ml of deionized water. All carbons used in the 16 tests were first neutralized by standing overnight in this amount and concentration of acid. Separate batch and continuous flow tests were conducted. In all cases, the pH of the two synthetic coal mine waters used for these tests was adjusted to 3.0 with sulfuric acid.

For the batch tests, the general procedure was essentially followed. A 16 g portion of the selected activated carbon was placed in a gas washing bottle with 150 ml of synthetic coal mine water. The concentration of Fe^{2+} in the water was either 100 or 1,000 mg/l depending on the particular test. The water was analyzed at specified periods of time during a 180-minute aeration period. Duplicate tests were performed immediately following the first test for each one of the 16. The carbon was rinsed with 50 ml of deionized water between duplicate tests.

For the column experiments, the general procedure was essentially followed. An 80 g portion of the selected activated carbon was placed in the 22 in. x 1 in. column. Air, at a rate of either 50 or 500 ml/min depending on the particular test, was introduced by means of a gas dispersion tube at the bottom of the column. Synthetic coal mine water, containing either 100 or 1,000 mg/l of Fe^{2+} depending on the particular test, flowed through the column at a rate of approximately 30 ml/min. Duplicate tests were performed immediately following the first test for each one of the 16. The carbon was rinsed with 250 ml of deionized water between duplicate tests.

Statistical Design II

This phase of the research program involved a study of the effects of changes in the concentration of several components of the synthetic coal mine water other than ferrous iron on removal of iron. These additional components included pH and concentrations of aluminum, manganese, and sulfate in the synthetic coal mine water, and another 2^4 factorial experiment was designed. The methodology involved in this factorial experiment was identical to that used in the Statistical Design I experiments. For each of the 16 tests, a fresh quantity of Nuchar WV-W carbon, 12 x 40 mesh, was soaked in deionized water overnight prior to use. The synthetic coal mine water contained approximately 250 mg/l of Fe^{2+}, added as ferrous sulfate. The pH was either 1.5 or 3.5 depending on the particular test and was adjusted with HCl, instead of H_2SO_4 as in previous tests, so that this adjustment would not change the sulfate concentration. The concentration of sulfate in the water was either approximately 450 mg/l from the ferrous sulfate or approximately 8,000 mg/l from the ferrous sulfate and the additional amount added as magnesium sulfate, $MgSO_4 \cdot 7H_2O$, depending on the particular test. The concentration of manganese was either approximately 25 mg/l or approximately 100 mg/l, added as manganous chloride, $MnCl_2 \cdot 4H_2O$, depending on the particular test. The concentration of aluminum in the synthetic coal mine water was either approximately 50 mg/l or approximately 200 mg/l, added as aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, depending on the particular test.

Initially, aluminum hydroxide was added to the synthetic coal mine water as the source of aluminum but it was observed that this material would not solublize readily even at the low pH (1.5) of the test. Aluminum nitrate was then used. No special precautions such as drying, etc., were taken with the chemicals which were added as hydrates. It was assumed that each chemical contained the exact amount of water of hydration as specified on the label, although some samples of the same chemical, e.g. $MgSO_4 \cdot 7H_2O$, appeared to be more hygroscopic than others.

Again, separate series of batch and continuous flow tests were conducted. Each series consisted of 16 tests.

For the batch tests, the general procedure was essentially followed. A 16 g portion of carbon was placed in a gas washing bottle with 150 ml of the particular synthetic coal mine water and the mixture aerated at a rate of 150 ml/min for 120 minutes. Duplicate tests were performed immediately following the first test for each of the series of 16 tests. The carbon was rinsed with 50 ml of deionized water between duplicate tests. In most cases, the concentrations of manganese, aluminum, and sulfate were also determined.

For the column experiments, the general procedure was followed and the 19 in. x 3 in. column and 800 g of activated carbon were used. The carbon-water mixture was aerated at a rate of 150 ml/min and synthetic coal mine water was permitted to flow through the column at a rate of approximately 30 ml/min for a total of 360 minutes. Duplicate tests were performed on the next day for each test of the series of 16. The carbon was soaked overnight in the column with deionized water, which was drained prior to the duplicate test. In most cases, the concentrations of manganese, aluminum, and sulfate were also determined.

Additional Statistical Design Tests

The results of the two factorial experiments labeled Statistical Design I and II indicated that certain variables affected or did not affect the removal of iron with activated carbon. Tests were conducted only at high and low levels of the selected variables. To more precisely define the effect of these variables, additional continuous flow tests were conducted. The procedure, apparatus, and carbons used were similar to those of Test No. 12 of the continuous flow Statistical Design II experiment. The results of each of these additional tests were compared with those of Test No. 12. The synthetic coal mine water for Test No.12 consisted of approximately 250 mg/l of Fe^{2+}, a high concentration of aluminum, 200 mg/l, a low concentration of manganese, 25 mg/l, a high concentration of sulfate, 8,000 mg/l, and a high pH, 3.5. Test No. 12 was selected for comparison purposes because the iron removal was relatively constant throughout the duration of that test and because its results were reproducible.

In the first of this series, the effect of pH over the range 1.5 to 3.5, the low and high values in the Statistical Design II experiment, was examined by conducting tests at pH 1.5, 2.0, 2.5, 3.0, and 3.5. The first test at pH 1.5 was not used in the evaluation of pH effect. The second test at pH 1.5 was used in the evaluation since past tests (BCR Project 2040) had shown a first test with a fresh sample of carbon to be different from each of the succeeding ones, and that the second and succeeding tests gave similar results until the carbon was spent. This was probably due to the elution of soluble material present in the carbon during the first test. The same 800 g portion of Nuchar WV-W carbon, 12 x 40 mesh, was used in each test of this series. The carbon was kept overnight between tests in the column filled with deionized water. Tests were conducted in the following sequence: pH 1.5, 1.5, 3.5, 2.0, 3.0, 2.5, and, finally 1.5 again. The last test at pH 1.5 demonstrated that the carbon performed similarly to the second test at pH 1.5 and was not rendered inactive during these tests.

Test No. 12 was repeated but this time with no manganese, no aluminum, and no sulfate in the synthetic coal mine water. In another series, sodium chloride replaced the sulfate in the synthetic coal mine water.

In the last of this series, Test No. 12 was again repeated but with no aeration and with nitrogen instead of air bubbled through the carbon-water mixture. These tests were repeated using actual coal mine water with aeration, no aeration, and with nitrogen or oxygen instead of air.

Effect of Bed Depth

The effect of depth of the bed of activated carbon on removal of iron was examined by conducting continuous flow tests using the 19 in. x 3 in. column according to the general procedure with the following exception: in five tests, the amount of Nuchar WV-W carbon, 12 x 40 mesh, used was 80, 260, 440, 620, and 800 g for a bed depth of 3.5, 9.2, 15.6, 21.9, and 27.9 cm, respectively. A new portion of carbon was used for each test. Two tests were conducted with each portion of carbon. The first of each of the two tests was conducted with a ratio of carbon to total volume of mine water of 1 g/13.5 ml. In other words, with 80 g of carbon used, the first test consisted of flowing 1080 ml of standard synthetic coal mine water through the column. This took 36 minutes at 30 ml/min. The first test with 800 g of carbon was conducted with 10,800 ml of water for a total test of 360 minutes duration. Each of the second tests was conducted for 360 minutes.

Effect of Column Diameter

The effect of diameter of the column on removal of iron with activated carbon was examined by conducting a series of continuous flow tests according to the general procedure with Nuchar WV-W carbon, 12 x 40 mesh, standard synthetic coal mine water, and three molded acrylic tubes of 3 in., 4 in., and 5 in. diameter. The tests were repeated using actual mine water.

Effect of Temperature

To examine the effect of temperature on removal of iron, three continuous flow tests were conducted according to the general procedure with the 19 in. x 3 in. column, Nuchar WV-W carbon, 12 x 40 mesh, and standard synthetic coal mine water at temperatures of 12, 21, and 30 C.

Use of Materials Other Than Carbon

In a series of continuous flow tests with the 19 in. x 3 in. column conducted according to the general procedure, activated alumina (Aluminum Company of America) was used in place of activated carbon with standard synthetic and actual coal mine waters, and charcoal briquettes (Cumberland Charcoal Corporation) were used with standard synthetic coal mine water.

Tests with Actual Coal Mine Waters

Two series of continuous flow tests with the 19 in. x 3 in. column were conducted, with Nuchar WV-W carbon, 12 x 40 mesh, essentially according to the general procedure. In the first series, the Tarrs coal mine water was used. In one test, the concentration of Fe^{2+} was supplemented in the raw water by adding ferrous sulfate to it. In the second series, a stream sample, collected at various points along a tributary of Little

Plum Creek, was used.

Effect of Bacteria

Samples of water collected from selected catalytic oxidation experiments were analyzed for the presence or absence of Thiobacillus ferrooxidans and Thiobacillus thiooxidans by the Most Probable Number Method. Dilutions of the reaction systems were prepared in Silverman and Lundgren 9K basal salts plus ferrous sulfate or elemental sulfur as the energy source. Each dilution series was monitored for at least several days for bacterial activity. The bacterial analyses were conducted under the supervision of Dr. Francis W. Liegey, Chairman, Biology Department, Indiana University of Pennsylvania.

Cultures of Thiobacillus ferrooxidans and Thiobacillus thiooxidans were also obtained from Dr. Liegey and used in combination with the activated carbon.

Tests with Bacteria-inoculated Water

Active cultures of Thiobacillus ferrooxidans and Thiobacillus thiooxidans were obtained from Indiana University of Pennsylvania. Both batch and continuous flow experiments with the 22 in. x 1 in. column were conducted according to the general procedure with Nuchar WV-W carbon, 12 x 40 mesh, with (a) standard synthetic coal mine water which was inoculated with Thiobacillus ferrooxidans, (b) standard synthetic coal mine water which was inoculated with Thiobacillus thiooxidans, and (c) standard synthetic coal mine water which was inoculated with a mixture of Thiobacillus thiooxidans and Thiobacillus ferrooxidans. In each case, the cultures were mixed with the standard synthetic coal mine water in a 10:1 water to suspension of culture ratio. The culture was used at the 48-hour growth period, upon recommendation of Dr. Liegey, who stated that this is the time at which the bacteria are at the peak of their growth curve.

Tests with Bacteria-inoculated Carbon

For the batch tests, 500 ml of an aqueous suspension containing an active culture of Thiobacillus ferrooxidans was added to 80 g of Nuchar WV-W carbon, 12 x 40 mesh, in a gas washing bottle, and the mixture aerated for 24 hours at a rate of about 50 ml/min. At the end of this time, the water was decanted from the mixture and replaced with standard synthetic coal mine water containing ferrous iron as an energy source for the bacteria. The procedure was repeated three times per week with continuous aeration for a total of 18 days. Another 80 g portion of Nuchar WV-W carbon was placed in a separate gas washing bottle. No bacteria were added to this carbon. The contents were treated in a manner identical to the carbon-bacteria, i.e., standard synthetic coal mine water was added at the same intervals and aeration continued; this carbon system was used as a blank for comparison of the results with the carbon-bacteria system. After 18 days of this treatment, the synthetic coal mine water was decanted from each of the carbons and replaced with 150 ml of fresh standard synthetic mine water. Aeration at 150 ml/min was continued for 120 minutes. Two 120-minute tests were conducted with each system.

For the first of the column tests, 500 ml of the same aqueous suspension of Thiobacillus ferrooxidans used in the batch tests was added to 80 g of Nuchar WV-W carbon, 12 x 40 mesh, in the 22 x 1 in. column. This mixture was aerated at about 75 ml/min for 24 hours. The water was drained from the bottom of the column and replaced with standard synthetic coal mine water as an energy source for the bacteria. As in the batch tests, the water was "changed" three times per week and aeration continued for 18 days. After this time, fresh synthetic mine water was placed in the column and a test conducted according to the general procedure for a total of 360 minutes.

To examine the long term effects of the iron-oxidizing bacteria-activated carbon combination, the carbon samples which had previously been treated with Thiobacillus ferrooxidans culture on September 30, 1971, and used in a batch test (80 g) and a continuous flow test (80 g) on October 15, 1971, which were just described, were combined in the 19 in. x 3 in. column, "fed" with ferrous sulfate solutions, additional Nuchar WV-W carbon added to this column in batches of 80 g to a total of 800 g of carbon, and the column aerated continually. Continuous flow tests were conducted with this column, which still contained iron-oxidizing bacteria, and with standard synthetic coal mine water. These tests were conducted on January 5, 1972, approximately two months after receipt of the original culture. A sample of the feed water drained from the column prior to this series of tests was sent to Dr. Liegey at Indiana University for evidence of survival of the bacteria. Seven tests were conducted according to the general procedure. Ferrous sulfate solution was added and the column aerated between tests to maintain the activity of the bacteria.

Effect of Long Aeration Periods Prior to Testing

A series of continuous flow tests in the 19 in. x 3 in. column were conducted with Nuchar WV-W carbon, 12 x 40 mesh, and with standard synthetic and actual coal mine waters using a bacteria-inoculated carbon and a carbon without bacteria to examine the effect on iron removal of aerating these carbons continually for long periods of time, in this case longer than one month, prior to their use. Similar tests were conducted using activated alumina instead of activated carbon.

Tests with Bacteria-inoculated Coal

Continuous flow tests were conducted with the 19 in. x 3 in. column according to the general procedure with actual coal mine water and coal being used in place of the activated carbon. The coal was inoculated with Thiobacillus ferrooxidans approximately 15 days prior to the tests and treated in the same manner as was the activated carbon.

Statistical Design III

This phase of the research program involved a study of the effects on removal of iron from an actual coal mine water of water flow rate, amount of carbon, bacteria versus no bacteria, and aeration rate. A 2^4 factorial experiment was designed. The methodology involved in this factorial experiment was identical to that used in Statistical Design I and II experiments. For eight of the 16 tests, a fresh quantity of Nuchar WV-W carbon, 12 x 40 mesh, was placed in a 19 in. x 3 in. column with deionized water and aerated for 24 hours prior to the test. The other eight of the 16 tests were conducted with a fresh supply of Nuchar WV-W carbon, 12 x 40 mesh, which had been placed in the column and inoculated with a suspension of Thiobacillus ferrooxidans. A new solution of standard synthetic coal mine water was added to the column every other day. The column was then used in a test approximately three weeks after the original inoculation.

The water flow rate was either 20 ml/min or 80 ml/min, the aeration rate was either 50 ml/min or 500 ml/min, and the amount of carbon was either 500 g or 1,000 g, depending on the particular test. For the 16 individual continuous flow tests, the general procedure was followed with the changes as indicated in the individual tests.

Effect of Water Flow Rate

In the first of this series, a sample of Nuchar WV-W carbon, 12 x 40 mesh, was used in a continuous flow test with a 22 in. x 1 in. column and standard synthetic coal mine water according to the general procedure. Then this same carbon was used in a series of tests essentially according to the general procedure but with water flows of 30, 100, 150, 200, 300, and 600 ml/min, respectively, for 90 minutes each.

In the second of this series, stream samples, collected at various points along a tributary of Little Plum Creek, were used. The effect of flow rate was examined by conducting continuous flow tests with a 19 in. x 3 in. column and Nuchar WV-W carbon, 12 x 40 mesh and at water flows of 30, 60, and 120 ml/min.

In the last of this series, the activated carbons, which were used in the Statistical Design III experiment and which contained Thiobacillus ferrooxidans, were combined for a total of approximately 6500 g of carbon. This carbon was placed in a 52 in. long x 5 in. inside diameter molded acrylic column similar to the other columns used on this project. The carbon filled this column to a depth of 34 in. The column was fed and aerated continually, similar to other columns containing bacteria, and then used in five tests with actual coal mine water according to the general procedure but with water flow rates of 20, 200, 400, 800, and 1600 ml/min.

SECTION V

RESULTS AND DISCUSSION

Effect of Variables

Past studies (1, 12, 13, 14, 15, 16) established that aeration of low pH acid mine drainage containing ferrous iron in the presence of activated carbon resulted in a significant decrease in concentration of ferrous iron, Fe^{2+}, in the water. Aeration of the same quality water in the absence of activated carbon resulted in no significant change in concentration of Fe^{2+} (See, particularly, Figure 16, p. 64 of Reference 1). To utilize this information in a practical mine drainage treatment process, a study of the variables influencing the oxidation of Fe^{2+} in acid mine drainage was undertaken.

Column Design

Initial tests were conducted with gas washing bottles and with a number of glass tubes used as columns to obtain information which was used to design a column or columns for this project. A variety of carbons were used in the glass tubes to establish flow rates of the water through the columns under various conditions. Then, the smallest-diameter column was used in a series of tests with synthetic coal mine water and activated carbon, Nuchar WV-W, to note the effect of aeration versus no aeration on the effectiveness of the column to oxidize (remove) iron. These effects were double checked by conducting similar batch tests with the gas washing bottles. The effects of both the method of packing the carbon and aeration by suction through the column were also examined.

Water Flow Rates through Column--A 22 in. x 1 in. glass column was charged with 100 g of BPL carbon, 4 x 10 mesh, and then filled with the standard synthetic coal mine water. With no aeration, flow by gravity into the top and out of the bottom of the column was 400 ml/min. With the 6 x 16 mesh BPL carbon, the flow rate was 300 ml/min; with the 12 x 30 mesh BPL carbon, 200 ml/min. There was a direct relationship between the particle size of the carbon and the flow rate. As expected, the smaller particles restricted the flow.

Next, a 19 in. x 3 in. glass column was charged with approximately 800 g of Nuchar WV-W carbon, 12 x 40 mesh, and then filled with the standard synthetic coal mine water. A maximum flow of 1030 ml/min was obtained with gravity flow. This corresponds to 390 gal/day. With larger columns and pumped water, it seemed probable that any desired flow could be obtained.

Effect of Aeration--Three sets of conditions were used in column experiments: (a) the synthetic coal mine water-carbon mixture was not aer-

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ated, (b) the water was aerated prior to entering the column, and (c) the water-carbon mixture was aerated in the column.

In the first series, involving no aeration, three separate tests were conducted with the 22 in. x 1 in. column, Nuchar WV-W carbon, 12 x 40 mesh, and the following flow-rates through the column: 150, 75, and 30 ml/min. On the basis of Fe^{2+}, as monitored during the test, flow rates of 150 and 75 ml/min were too fast for effective iron removal. Even at 30 ml/min, the effectiveness of removal falls off drastically after 30 minutes.

Batch tests were conducted to check the results of the column tests. As in the column tests, the oxidation (removal) of Fe^{2+} in the non-aerated systems was unsatisfactory in all cases.

In the next series, the standard synthetic coal mine water was aerated by means of a gas dispersion tube before it was passed through the column. If aeration of the mine water prior to its passing through the column would result in satisfactory removal of Fe^{2+}, then a simpler column could be designed and utilized for this program. For these tests, Darco carbon, 4 x 12 mesh, and the 22 in. x 1 in. column were used. The water was held and aerated for 3 min and then flow started through the column at 30 ml/min. Aeration of the water before it entered the column was continued for the duration of the test. A duplicate test was conducted using Darco carbon, 4 x 12 mesh, and an additional one using Nuchar WV-W carbon, 12 x 40 mesh. As in the case of the tests with no aeration, the effectiveness of these carbons decreased after a very short period of time.

Batch tests with Darco and Nuchar WV-W were also conducted to check the results of the column tests. As in the column tests, aerating the water prior to contact with the carbon produced unsatisfactory results in terms of the removal of Fe^{2+}.

In the final series, aeration was carried out by means of a gas diffuser directly in the column (with appropriate venting of the column). In duplicate experiments, Darco carbon, 4 x 12 mesh, and the 22 in. x 1 in. column were used. The flow rate of the synthetic coal mine water was 30 ml/min and air flow rate was 150 ml/min. Effectiveness of iron removal with Darco was no better than in the tests with no aeration and aeration outside of the column. But in similar tests with Nuchar WV-W carbon, 12 x 40 mesh, the effectiveness was improved. In these same tests with Nuchar WV-W carbon, either the water was introduced at the top of the column and air introduced at the bottom opposite to the flow of the water, or air was introduced at the top of the column with the water. In the latter case, with no vent at the top of the column, the air then flowed down through the carbon-water mixture and out of the bottom of the column. Aerating through the top was less effective in removing iron than was aerating through the bottom.

In the next test, the 53.5 in. x 1.5 in. column was charged with approximately 400 g of Nuchar WV-W carbon, 12 x 40 mesh. The synthetic coal mine water was introduced at the top of the column at a rate of 35 ml/min and air introduced at the bottom at a rate of 150 ml/min.

More effective removal of iron was demonstrated with the longer column containing more carbon, partially due to the higher pH as a result of the greater amount of carbon. During the test, the iron removal decreased with decreasing pH as the carbon contacted more and more water. This implies oxidation of Fe^{2+} as the factor controlling iron removal since more iron would be oxidized at the higher pH values. The rate of oxidation increases a hundredfold with each increasing pH unit (5, 6), but adsorption, which might also be influenced by pH, could not be excluded.

Again, to check these results, similar batch tests were performed with the gas washing bottle. The results of one of these tests and a continuous flow test with Nuchar WV-W are presented in Table 1. In the batch test, the concentration of Fe^{2+} decreased to about 3 mg/l after 10 minutes. The time of contact between water and carbon in the column was much shorter; therefore, the decrease in Fe^{3+} from the continuous flow test was not so dramatic as in the batch test. The results of the batch test, as presented in Table 1, illustrated the type of effects of activated carbon on Fe^{2+} which led to this project. Aeration of the same water at the same low pH with no activated carbon present would have resulted in no change in the concentration of Fe^{2+} as compared to about 240 mg/l of Fe^{2+} in less than 10 minutes from the data in Table 1.

Effect of Method of Packing the Column -- The method of packing the column was examined. The column was charged with Nuchar WV-W carbon, 12 x 40 mesh, which had been boiled previously in one liter of deionized water. Filling the column with the carbon-water mixture was accomplished so that the carbon was immersed in water at all times prior to the test. Compared to the use of a column which was packed with dry carbon, using this wet, previously boiled carbon resulted in more effective removal of Fe^{2+} for about the first 30 minutes of treatment. After that time, however, the effectiveness of each column was the same regardless of method of packing.

Effect of Aerating by Suction--A unique column was used by the Bureau of Mines (16) for short duration batch tests to oxidize ferrous iron with activated carbon. The size of that column was similar to one used in this work, the principal difference being that in the Bureau's tests, the water was pulled down through the column by suction. This also served to accomplish aeration of the carbon-water mixture. In the work reported here, the water flows by gravity or can be pumped into the top of the column; air is introduced into the bottom of the column and excess air vented through the top. Either configuration

TABLE 1. PRELIMINARY TESTS FOR EFFECT OF AERATION ON FERROUS IRON REMOVAL

Time, min	Continuous Flow Test Experiment No. 433-30 Fe^{2+}, mg/l	Batch Test Experiment No. 434-21 Fe^{2+}, mg/l
0	251	245
5	10	45
10	23	3
15	39	3
30	64	2
45	89	2
60	110	2
75	125	0
90	140	0
105	-	0
120	-	0
135	-	0
150	-	0
165	-	0
180	-	0

would present some problems in adaptation to a continuous flow system as long as some form of aeration is necessary.

The results of a BCR continuous flow test are presented in Table 2 and compared with the Bureau's results. At the end of their test of 2.6 minutes duration, 98.2 percent of the original Fe^{2+} has been removed. At the end of 5 minutes in the BCR tests, 96.6 percent of the original Fe^{2+} had been removed. But in the BCR tests, which were of a much longer duration, there was a gradual decrease in effectiveness of iron removal with time. There was no difference in effectiveness of removal of iron when aeration was accomplished by suction.

Role of Adsorption

During the tests on column design which were described in the previous section, there was also a decrease in concentration of total iron, Fe_T, which includes both ferrous, Fe^{2+}, and ferric, Fe^{3+}, iron. This was an indication that adsorption of iron may play a role in the mechanism for iron removal since removal by oxidation would result in a decrease in concentration of Fe^{2+} with no change in concentration of Fe_T. Adsorption of Fe^{2+} onto the surface of the activated carbon without oxidation to the Fe^{3+} state in an actual treatment operation might be detrimental to the effectiveness of this method of iron removal since back-washing of the carbon would redeposit Fe^{2+} back to the stream. Any advantage gained would be in concentrating the iron and thereby treating a smaller volume of water. Assuming then that only adsorption and no oxidation had taken place, experiments were conducted to measure the adsorptive capacity of Nuchar WV-W carbon.

Determination of the Freundlich Adsorption Isotherm -- Aliquots of standard synthetic coal mine water and samples of Nuchar WV-W carbon, 12 x 40 mesh, were agitated as described in the Experimental section and the water analyzed for Fe^{2+} and Fe_T. The weight of carbon, M, and the concentration of Fe^{2+} remaining in solution at the end of 60 minutes, C, were used in the Freundlich adsorption equation (25):

$$\frac{X}{M} = KC^{\frac{1}{n}}$$

where X = units of Fe^{2+} removed

M = weight of carbon required to remove X

C = concentration of Fe^{2+} remaining in solution

K,n = constants

TABLE 2. COMPARISON OF BCR AND BUREAU OF MINES RESULTS OF CONTINUOUS OXIDATION OF FERROUS IRON

Time, min	BCR Experiment No. 433-37 Fe^{3+}, mg/l	Bur. of Mines Experiment No. 65 (Ref. 16) Fe^{3+}, mg/l
0	250	830
2.6	-	15
5	6	-
10	50	-
15	83	-
30	122	-
45	143	-
60	153	-
75	148	-
90	163	-
105	163	-
120	166	-
135	167	-
150	168	-

The equation can also be stated in logarithmic form

$$\log \frac{X}{M} = \log K + \frac{1}{n} \log C$$

which is the equation of a straight line. The data were plotted, but a straight line was not obtained, probably because some oxidation occurred concurrently with adsorption.

The experiment was repeated with the minus 325 mesh fraction of Nuchar WV-W carbon since the Freundlich equation more properly applies to powdered carbons. The results were essentially identical.

Adsorption-Acid Extractions--One sample of carbon was treated with 50 ml of standard synthetic coal mine water and a second sample with deionized water as described in the Experimental section. Originally, 50 ml of the synthetic contained 241 mg/l of Fe^{2+} or an input to the system of 12 mg of Fe^{2+}. Carbon containing the adsorbed iron was washed with hot HCl. Analysis of the acid wash accounted for 5.7 mg of Fe^{2+}, or less than 50 percent of the Fe^{2+} originally used. The same type of calculation was done with Fe_T; in that case, only 60 percent of the total iron was accounted for. It could not be established from this test whether any oxidation of Fe^{2+} to the Fe^{3+} state accompanied the adsorption since, surprisingly, some of the iron remained on the carbon, even after extraction with hot acid.

The test was repeated and this time the carbon was washed (a) with 25 ml of hot (80-90 C) 6N HCl, (b) again with 25 ml of hot 6N HCl and (c) a third time with 25 ml of hot 6N H_2SO_4. The total amount recovered by these acid extractions was surprisingly similar to that from the first experiment. The carbon apparently clings tenaciously to part of the adsorbed iron.

Comparison of Adsorption of Fe^{2+} and Fe^{3+}-- To determine the rates of adsorption of Fe^{2+} and Fe^{3+} on activated carbon, identical batch tests were conducted with activated carbon and with solutions of (a) Fe^{2+} - ferrous sulfate adjusted to pH 3.0 with sulfuric acid and (b) Fe^{3+} - ferric nitrate with pH 2.5 without adjustment. A comparison was then made of the differences between the rate of adsorption of each species. A plot of the log of concentration of iron versus time from the data obtained is shown in Figure 3. The differences in the rate of adsorption of each species are evident. In addition, the reasonable "fit" of the data by the method of least squares to a straight line indicates that the rate of adsorption in each case is first-order with respect to the concentration of that particular species,

$$-\frac{d\,[Fe]}{dt} = k\,[Fe]$$

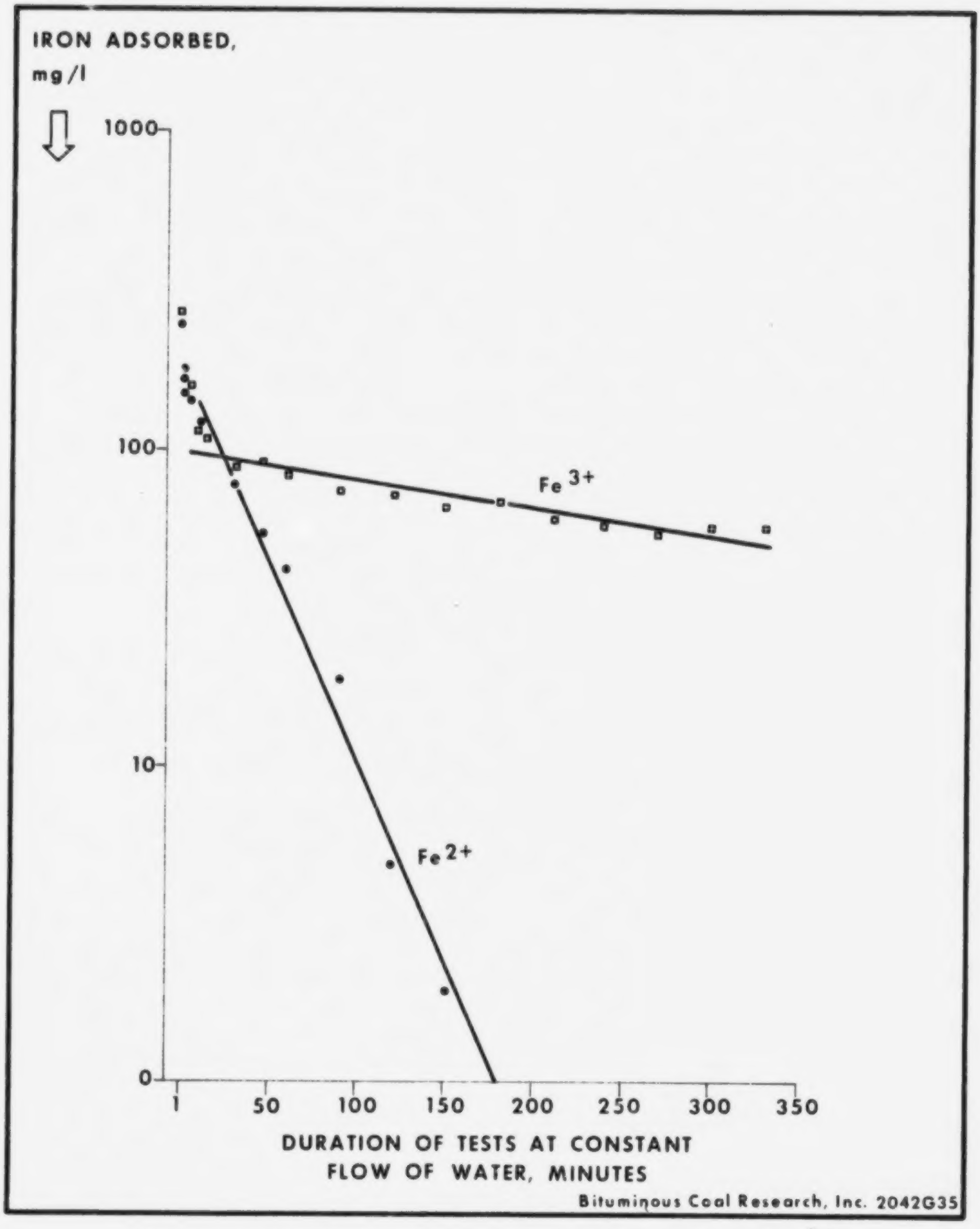

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Figure 3. Comparison of Rates of Adsorption of Fe^{2+} and Fe^{3+} on Activated Carbon

Effect of pH on Adsorption of Fe^{2+} and Fe^{3+} -- The studies just described have shown that there was a difference between the rate of adsorption of Fe^{2+} and Fe^{3+} on the surface of activated carbon. In those studies, no effort was made to measure the rates of adsorption from solutions having the same pH or to control the pH throughout the duration of the tests. In this series of batch tests, pH was controlled throughout the tests. The results of the tests to measure the adsorption of Fe^{2+} on activated carbon over the range of pH values most encountered in those actual coal mine waters to be neutralized are listed in Table 3. It can be seen from the data in this table that iron was adsorbed more rapidly at the higher pH values.

These data were then used in developing rate curves for adsorption of Fe^{2+} by plotting the log of the concentration of Fe^{2+} remaining in solution versus time for each of the tests at the pH values listed. These are shown in Figure 4. It can be seen from Figure 4 that there was not much difference in the rate of adsorption of Fe^{2+} from pH 1.0 to 2.5. There was a substantial increase, though, in this rate between 2.5 and 3.0. In fact, the test at pH 2.7 was conducted after this graph was originally drawn and the rate curve for this pH value was then drawn as anticipated. From pH 3.0 to 5.0 there is a less rapid but still substantial increase in this rate. From these data, a process for removal of iron based solely on adsorption of Fe^{2+} might be applicable only to those actual coal mine waters having a pH greater than 2.5. In reality, very few coal mine waters have a pH below 2.5.

The data from Table 3 and Figure 4 were used in the calculation of the amount of Fe^{2+} adsorbed per hour with pH and these data are plotted in Figure 5. From this figure the amount of iron adsorbed per hour can be determined for any pH value over the range 1.0 to 5.0.

The results from tests to measure the adsorption of Fe^{3+} on activated carbon over the pH range of 1.0 to 5.0 are presented in Table 4. The concentration of Fe^{3+} was then calculated by subtracting Fe^{2+} and Fe_T and these concentrations are listed in Table 5. The data in Table 5 seem to indicate a more rapid adsorption of Fe^{3+} on activated carbon at pH 1.0, 2.0, and 2.5 than at the higher pH values. Closer examination of the data in Table 4, however, reveals a substantial reduction of Fe^{3+} to Fe^{2+} occurring in the solutions of ferric nitrate at these low pH values. A plot of the data in Table 5 showing the log of the concentration of Fe^{3+} remaining in the solution versus time, as seen in Figure 6, indicates little differences in the rates of adsorption of Fe^{3+} at the pH values listed, at least as compared to the differences shown in Figure 4 for rates of adsorption of Fe^{2+} as affected by pH. The adsorption rates of Fe^{3+} are complicated by the appearance of Fe^{2+} with time in the ferric nitrate as shown in Table 4. A plot of the log of the concentration of Fe^{2+} in solution versus time (from Table 4) is shown in Figure 7. There is a strong resemblance of this data to that in Figure 4. This indicates that the Fe^{2+} is produced by reduction of Fe^{3+} at the start of the test and that

TABLE 3. ADSORPTION OF Fe^{2+} ON ACTIVATED CARBON

Time, min	Fe^{2+} Remaining in Solution, mg/l						
	Experiment Number 440-93 pH 1.0	Experiment Number 440-85 pH 2.0	Experiment Number 440-83 pH 2.5	Experiment Number 440-97 pH 2.7	Experiment Number 440-91 pH 3.0	Experiment Number 440-89 pH 4.0	Experiment Number 440-95 pH 5.0
0	205	234	231	221	244	237	227
5	179	179	156	91	117	81	94
10	182	195	159	104	91	68	75
15	188	211	195	120	84	65	55
30	188	201	179	117	62	36	19
45	195	208	172	120	39	16	10
60	182	172	156	114	36	6	0
90	172	143	156	71	23	6	0
120	166	127	114	55	3	0	0
150	156	110	91	39	0	0	0
180	140	110	78	26	0	0	0
210	84	104	81	19	0	0	0
240	75	101	81	13	0	0	0
270	68	97	78	6	0	0	0
300	62	78	75	0	0	0	0

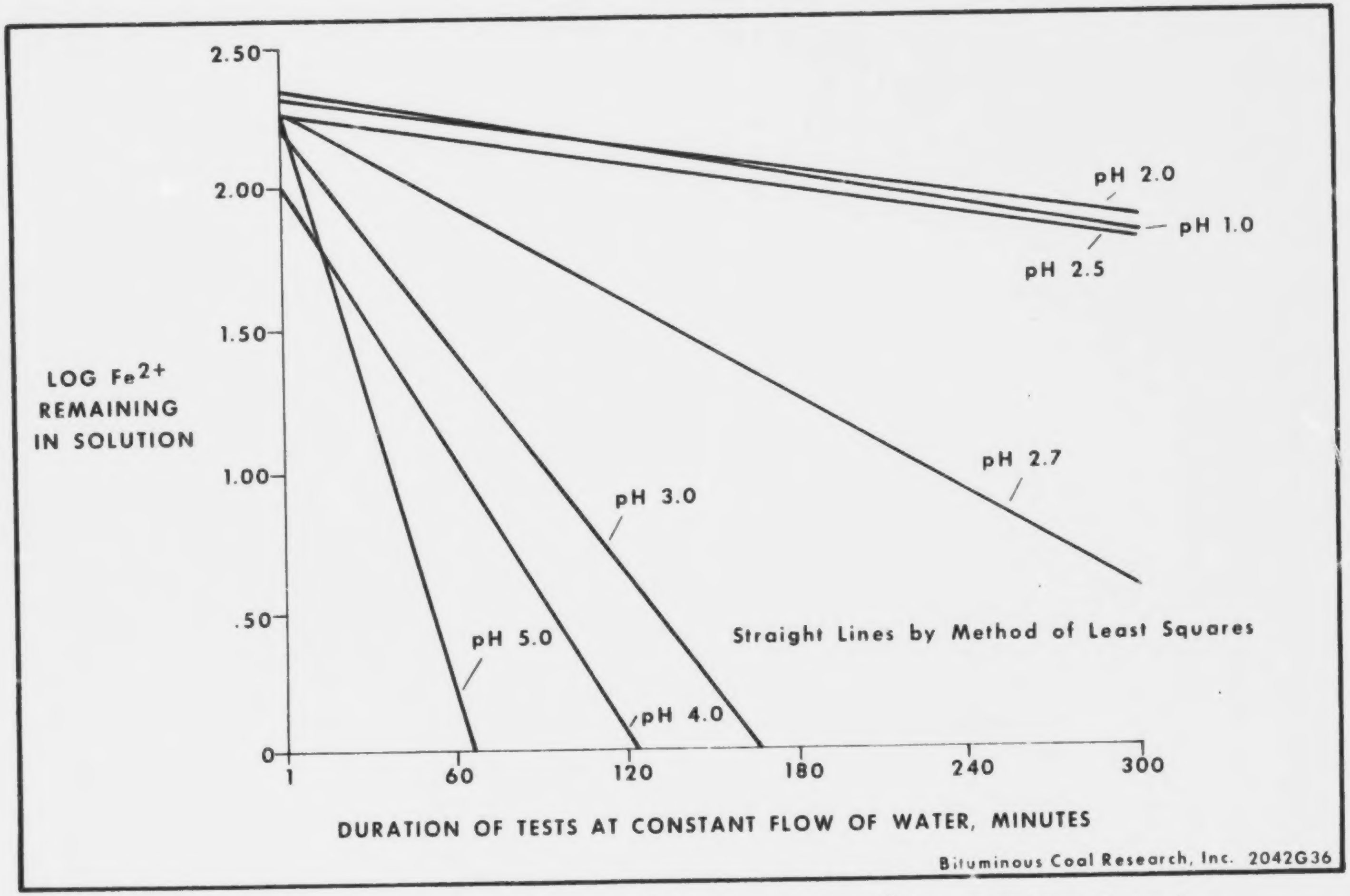

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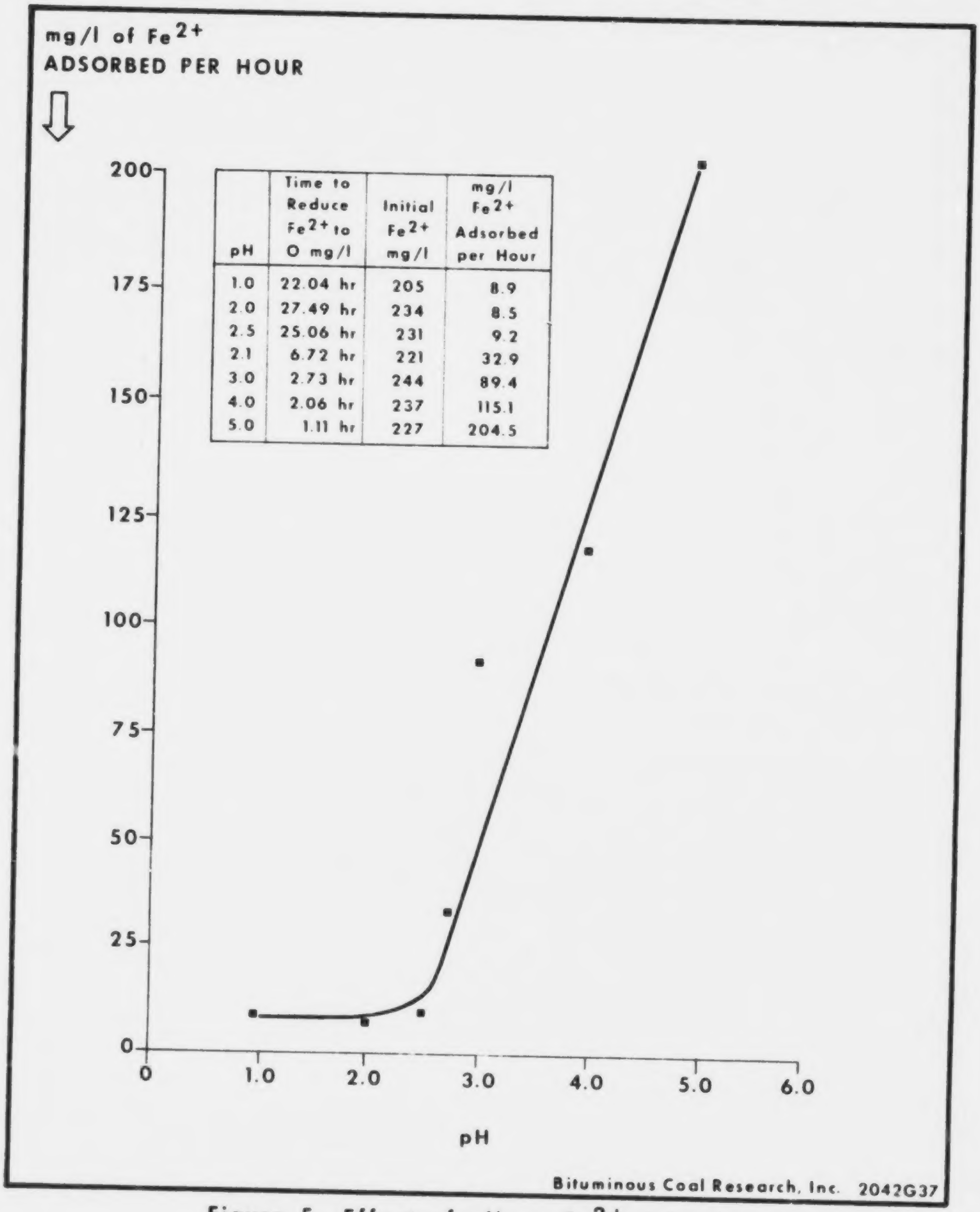
Figure 4. Effect of pH on Rate of Adsorption of Fe^{2+} on Activated Carbon



pH	Time to Reduce Fe^{2+} to 0 mg/l	Initial Fe^{2+} mg/l	mg/l Fe^{2+} Adsorbed per Hour
1.0	22.04 hr	205	8.9
2.0	27.49 hr	234	8.5
2.5	25.06 hr	231	9.2
2.1	6.72 hr	221	32.9
3.0	2.73 hr	244	89.4
4.0	2.06 hr	237	115.1
5.0	1.11 hr	227	204.5

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Figure 5. Effect of pH on Fe^{2+} Adsorbed per Hour on Activated Carbon

TABLE 4. ADSORPTION OF Fe^{3+} ON ACTIVATED CARBON. I.

Time, min	Experiment Number 440-94 pH 1.0		Experiment Number 440-86 pH 2.0		Experiment Number 440-84 pH 2.5		Experiment Number 440-98 pH 2.7		Experiment Number 440-92 pH 3.0		Experiment Number 440-90 pH 4.0		Experiment Number 440-96 pH 5.0	
	Fe^{3+} mg/l	Fe_T mg/l	Fe^{3+} mg/l	Fe_T mg/l	Fe^{3+} mg/l	Fe_T mg/l	Fe^{3+} mg/l	Fe_T mg/l	Fe^{3+} mg/l	Fe_T mg/l	Fe^{3+} mg/l	Fe_T mg/l	Fe^{3+} mg/l	Fe_T mg/l
0	0	247	0	250	3	244	6	237	0	244	0	244	0	256
5	211	244	172	205	123	135	16	201	16	240	10	244	19	240
10	185	237	179	218	120	188	36	188	13	227	10	221	3	221
15	172	247	182	227	133	188	42	198	13	221	0	224	0	231
30	182	256	195	227	140	185	52	185	13	211	0	234	0	221
45	172	247	192	214	146	185	49	192	13	224	0	227	0	211
60	172	256	140	208	140	185	32	195	10	227	0	221	0	224
90	146	240	120	198	143	185	42	182	3	234	0	234	0	237
120	107	244	104	188	117	175	32	175	0	227	0	211	0	227
150	94	247	104	185	94	166	23	169	0	224	0	211	0	227
180	75	247	91	166	81	146	19	159	0	224	0	211	0	221
210	71	234	91	166	65	146	19	162	0	211	0	221	0	227
240	62	240	94	159	71	149	16	162	0	208	0	234	0	231
270	62	244	84	162	71	146	16	159	0	179	0	224	0	231
300	55	244	68	156	68	143	16	156	0	133	0	214	0	237

TABLE 5. ADSORPTION OF Fe^{3+} ON ACTIVATED CARBON II

Time, min	Fe^{3+} Remaining in Solution, mg/l						
	pH 1.0	pH 2.0	pH 2.5	pH 2.7	pH 3.0	pH 4.0	pH 5.0
0	241	250	241	231	244	244	256
5	33	33	62	185	224	234	221
10	52	39	68	152	214	211	218
15	75	45	55	156	208	224	231
30	74	32	45	133	198	234	221
45	75	22	39	143	211	227	211
60	84	68	45	163	217	221	224
90	94	78	42	140	231	234	237
120	137	84	58	143	227	211	227
150	153	81	72	146	224	211	227
180	172	75	65	140	224	211	221
210	163	75	81	143	211	221	227
240	178	65	78	146	208	234	231
270	182	78	75	143	179	224	231
300	189	88	75	140	133	213	237

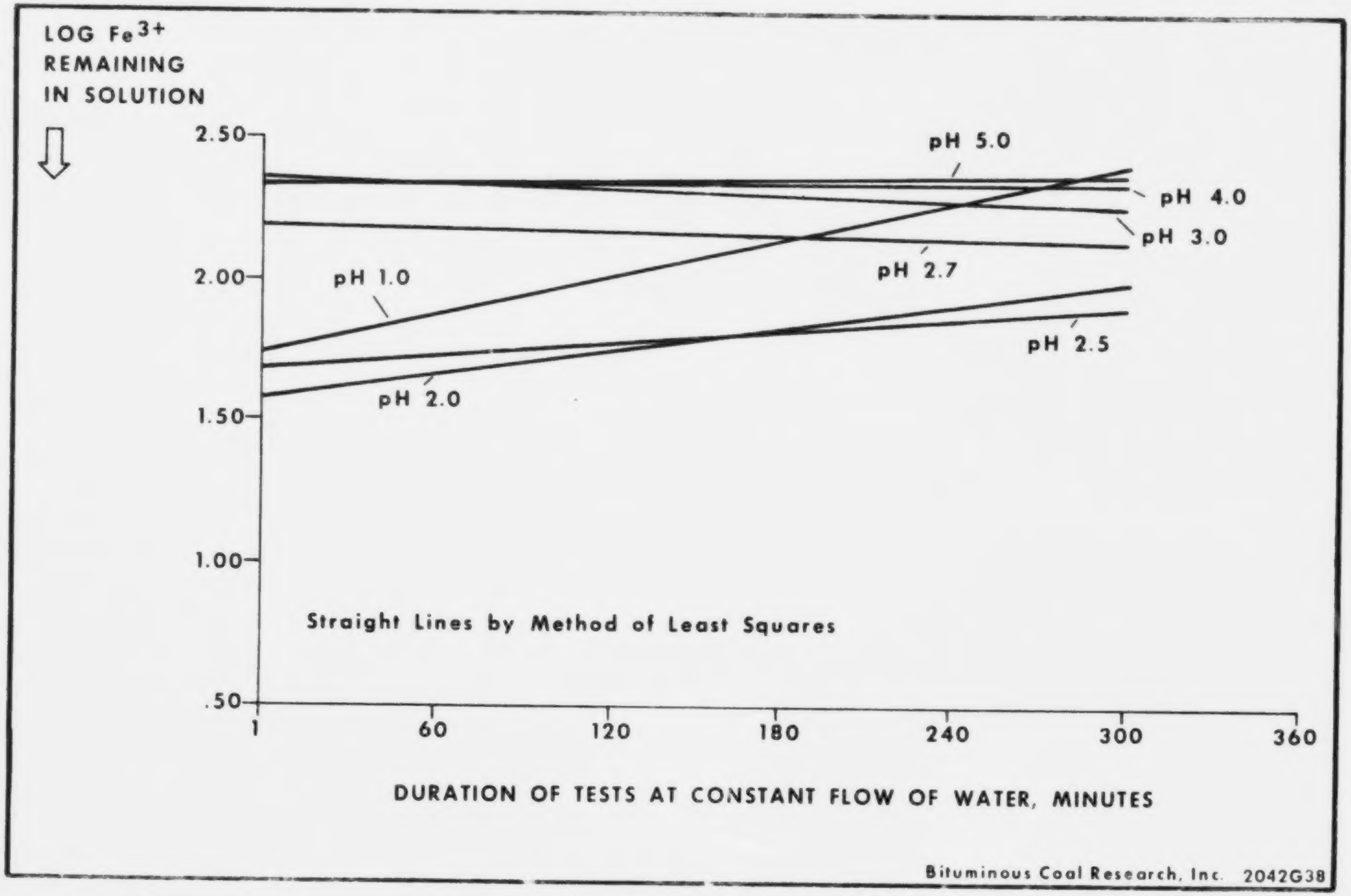

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Figure 6. Effect of pH on Rate of Adsorption of Fe^{3+} on Activated Carbon

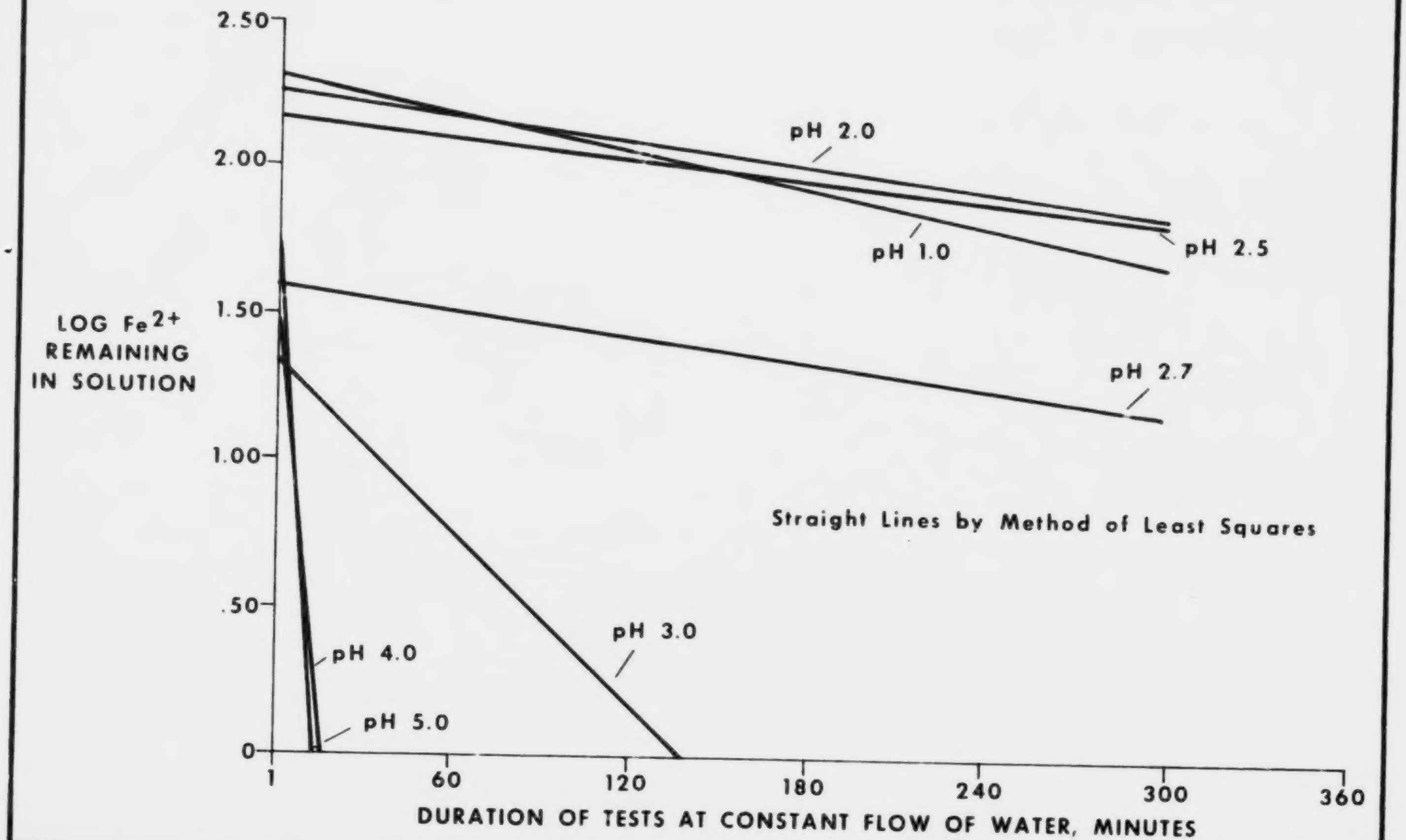

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Figure 7. Concentration of Fe^{2+} from Reduction of Fe^{3+} during Adsorption Tests

what is plotted in Figure 7 represents the adsorption of this Fe^{2+} with time on the activated carbon.

From Table 4, the concentration of Fe^{2+} produced in 5 minutes by the reduction of Fe^{3+} was plotted versus the initial pH in Figure 8. It can be seen from this figure that more Fe^{2+} was produced from the reduction of Fe^{3+} at the lower pH values. Again, as in the adsorption of Fe^{2+}, the pH value of 2.5 is important, since, below that value, the reduction of iron to the ferrous, Fe^{2+}, state proceeds at a relatively rapid rate.

Reduction of Iron

Because of the unexpected reduction of ferric iron, Fe^{3+}, to the ferrous state, Fe^{2+}, which occurred during the previously described experiments, batch and continuous flow experiments were conducted with a synthetic coal mine water containing approximately 250 mg/l of ferric iron, Fe^{3+}, added as ferric nitrate and having a pH of 2.5.

Batch Tests -- Tests were conducted with 16 g of Nuchar WV-W carbon, 12 x 40 mesh, which had previously been washed with two 20 ml portions of 6N HCl and two 20 ml portions of deionized water. Other tests were conducted with carbon which was not acid-washed and carbon which was washed with H_2SO_4 instead of HCl. The results of typical tests are presented in Table 6. Duplicate tests gave essentially identical results. In every instance, Fe^{3+} was reduced to the Fe^{2+} state even though the experimental conditions, including aeration, would seem more conducive to oxidation. The acid-washed carbons were more effective reducing agents in these tests than the carbon that was not acid-washed. Little difference in effectiveness was noted between carbons washed with HCl and H_2SO_4, although the HCl-washed carbons were slightly more effective reducing agents.

Continuous Flow Tests -- In a manner similar to the batch tests, tests were conducted with the column and "ferric" synthetic coal mine water according to the general procedure. The first test was conducted with carbon which had been washed with HCl. The results are listed in Table 7. As in the batch tests, reduction of Fe^{3+} to the Fe^{2+} state was observed. The test was repeated with carbon which had not been acid-washed. The results are also presented in Table 7. This time no reduction occurred until the relatively basic, soluble portion of the carbon was removed by elution. Below pH 6, reduction of iron was apparent and continued for the duration of the test. Both the batch and continuous flow tests resulted in the reduction of Fe^{3+} to Fe^{2+} and the extent of this reduction was dependent on the pH of the water.

Types of Carbon

Six different types of carbon having different origins were evaluated for this process by using each in both batch and continuous flow tests to relate the type of carbon to effective iron removal.

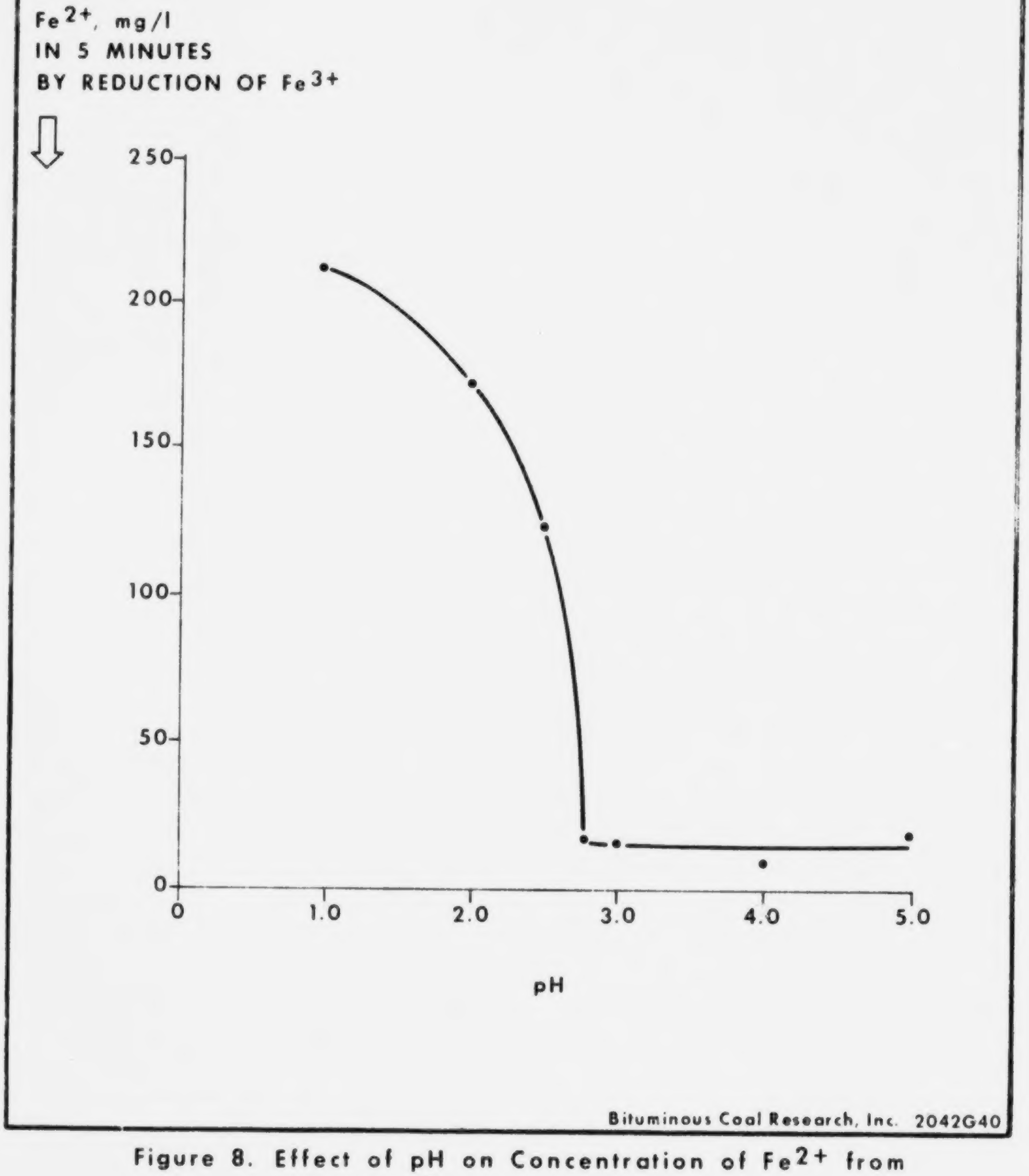

Figure 8. Effect of pH on Concentration of Fe^{2+} from Reduction of Fe^{3+} during Adsorption Tests

TABLE 6. REDUCTION OF IRON. BATCH TESTS.

Time, min	Experiment No. 434-56; Carbon Washed with HCl		
	pH	Fe^{2+}, mg/l	Fe_T, mg/l
0	2.5	0	247
5	-	158	231
10	-	163	-
15	-	163	227
30	-	194	-
45	-	205	219
60	2.4	201	221

Time, min	Experiment No. 434-58; Carbon Not Acid Washed		
	pH	Fe^{2+}, mg/l	Fe_T, mg/l
0	2.5	0	247
5	-	127	211
10	-	116	200
15	-	103	185
30	-	85	150
45	-	49	128
60	4.1	42	115

Time, min	Experiment No. 434-62; Carbon Washed with H_2SO_4		
	pH	Fe^{2+}, mg/l	Fe_T, mg/l
0	2.5	0	249
5	-	144	215
10	-	148	199
15	-	146	198
30	-	143	195
45	-	145	192
60	2.0	140	196

TABLE 7. REDUCTION OF IRON. CONTINUOUS FLOW TESTS.

	Experiment No. 433-54; Acid Washed Carbon		
Time, min	pH	Fe^{2+}, mg/l	Fe$_T$, mg/l
0	2.5	1	258
5	2.6	185	250
10	2.9	212	233
15	3.0	215	223
30	3.2	217	228
45	3.2	222	233
60	3.1	228	235
90	2.7	231	256
120	2.6	232	236
150	2.5	230	233

	Experiment No. 433-56; Carbon Not Acid Washed		
Time, min	pH	Fe^{2+}, mg/l	Fe$_T$, mg/l
0	2.5	0	251
5	8.5	0	8
10	7.3	0	5
15	6.3	0	26
30	5.7	95	100
45	5.4	118	158
60	4.9	140	173
90	4.6	200	220
120	4.6	209	233
150	3.0	220	259

Batch Tests -- The carbons used, their origin, and the results of the batch tests are summarized in Table 8.

From the results on both Fe^{2+} and Fe_T remaining after 60 and after 90 minutes in the second test, it can be seen that the bituminous coal-derived carbons were most effective in removing iron in this series. Lignite-, petroleum-, and coconut-derived materials were less effective. The mineral-derived carbon (manufacturer's description) was completely ineffective.

Continuous flow tests -- The same six carbons used in the batch tests were also used in continuous flow tests although some particle size fractions were slightly different than those used in the batch tests. The data from the continuous flow tests are summarized in Table 9 along with the carbons and their origin. The carbon which removed iron most effectively during the first 120 minutes of the test, while the flow rate was 30 ml/min, was a lignite-derived material. The two bituminous coal-derived carbons were next in effectiveness. These results are similar to those from the batch tests with the same carbons. In the batch tests, the lignite-derived material showed a substantial decrease in effectiveness when the same portion of that carbon was used in a second test.

After the initial 120 minutes of these tests, the flow was increased from 30 ml/min to 200 ml/min for an additional 30 minutes; then the flow was increased to the maximum attainable for each carbon with this system. Only Darco, 4 x 40 mesh, the lignite-based carbon, and Witco Carbon, 4 x 16 mesh, restricted the flow through the column. At the increased flow rates, no carbons removed iron effectively.

From the relatively small differences between Fe^{2+} and Fe_T concentration for most samples taken during both the batch and continuous flow tests (See Tables 8 and 9), adsorption of iron seems to be the mechanism indicated for removal of iron during these tests. Removal by oxidation alone would result in low Fe^{2+} values with little or no change in the Fe_T concentration from the original synthetic coal mine water -- in other words, relatively large differences between Fe^{2+} and Fe_T. A combination of adsorption-oxidation, though, cannot be eliminated as a possibility since that portion of the original Fe^{2+} concentration which might have been oxidized to the Fe^{3+} state may possibly also undergo rapid hydrolysis. The ferric iron compound thus formed could be precipitated even at relatively low pH. The end effect would again be relatively small differences between Fe^{2+} and Fe_T concentration, as were observed during these tests.

In summary, the results of both batch tests and continuous flow tests, indicate that the bituminous coal-derived carbons were the most effective carbons for removing iron. The lignite-derived material, though initially most effective, decreased in effectiveness with time and restricted the flow through the column.

TABLE 8. COMPARISON OF TYPES OF CARBON. BATCH TESTS

Carbon	Origin	Mesh Size	First Test**						Second Test**					
			After 5 min		After 60 min		After 120 min		After 5 min		After 60 min		After 90 min	
			Fe^{2+}*	Fe_T*	Fe^{2+}*	Fe_T*	Fe^{2+}*	Fe_T*	Fe^{2+}*	Fe_T*	Fe^{2+}*	Fe_T*	Fe^{2+}*	Fe_T*
Barnebey-Cheney AE	coconut shell	4 x 6	229	230	90	101	28	33	240	241	156	173	123	134
Witco Chemical	petroleum	4 x 10	217	222	73	91	12	32	222	234	134	141	82	89
Westvaco Nucher WV-W	bituminous coal	8 x 30	189	198	9	23	0	6	202	208	33	36	2	4
Pittsburgh Activated Carbon BPL	bituminous coal	6 x 16	190	192	1	17	0	8	195	198	32	39	0	9
Atlas Darco	lignite	4 x 12	178	185	1	27	1	2	191	209	70	96	29	34
Barnebey-Cheney 274	mineral	3 x 8	234	241	240	242	241	245	244	248	238	246	244	248

* All Fe^{2+} and Fe_T concentrations are expressed as milligrams per liter (mg/1).

** With synthetic coal mine water: pH, 3.0; Fe^{2+}, 244 mg/1; Fe_T 257 mg/1

TABLE 9. COMPARISON OF TYPES OF CARBON. CONTINUOUS FLOW TESTS

			Flow Rate, 30 ml/min						Flow Rate, 200 ml/min				Maximum Flow Attainable	
			After 5 min**		After 60 min		After 120 min		After 135 min		After 150 min		After 155 min	
Carbon	Origin	Mesh Size	Fe^{2+}*	Fe_T*	Fe^{2+}*	Fe_T*	Fe^{2+}*	Fe_T*	Fe^{2+}*	Fe_T*	Fe^{2+}*	Fe_T*	Fe^{2+}*	Fe_T*
Barnebey-Cheney AE	coconut shell	4 x 6	50	88	88	115	138	150	228	252	240	253	228	262
Witco Chemical	petroleum	4 x 16	20	33	88	117	170	202	239	288	252	278	262	268
Westvaco Nuchar WV-W	bituminous coal	8 x 30	25	45	43	68	115	138	228	250	232	245	238	248
Pittsburgh Activated Carbon BPL	bituminous coal	6 x 16	75	95	80	103	123	170	225	258	245	262	247	265
Atlas Darco	lignite	4 x 40	30	60	45	63	90	110	198	212	215	227	241	262
Barnebey-Cheney 274	mineral	3 x 8	222	250	238	265	238	262	238	262	238	262	233	252

* All Fe^{2+} and Fe_T concentrations are expressed as milligrams per liter (mg/l).

** With synthetic coal mine water: pH, 3.0; Fe^{2+}, 262 mg/l; Fe_T, 280 mg/l.

Statistical Design I

Both batch and continuous flow tests were conducted to examine the effects of particle size and surface area of the carbon as well as aeration rate and concentration of ferrous iron in the synthetic coal mine water on removal of iron, whether by oxidation, adsorption, or a combination of the two. A 2^4 factorial design was selected. The 16 tests required that an adequate supply of one type of carbon be available in two distinct and separate surface area ranges and two distinct and separate particle size ranges. After rejecting the use of many of the carbons solicited for this project, either because they did not meet the criteria established for these particular tests or because the properties were not always as represented on the labels, Filtrasorb 100 and Filtrasorb 300 were selected since (a) they are both coal-based carbons, (b) the surface area of Filtrasorb 100 is reported to be 800 m^2/g, of Filtrasorb 300, 950-1100 m^2/g, and (c) they were received in sufficient quantity in 8 x 40 mesh particle size so that an 8 x 10 and a 20 x 40 mesh particle size fraction could be obtained by screening. The aeration rates selected were 50 and 500 ml/min; the concentrations of Fe^{2+} in the synthetic coal mine water (at pH 3.0) were 100 and 1000 mg/l.

A preliminary batch test with Filtrasorb 100 conducted according to the conditions of one of the 16 factorial tests resulted in the synthetic coal mine water having a pH of 6.9 after one 2-hour test and 7.8 after a duplicate test. In each case there was no Fe^{2+} remaining in solution. Similar results were obtained with Filtrasorb 300. Since oxidation is dependent on pH (5, 6) and this process as envisioned involves oxidation at low pH, a high pH caused by the relatively basic, soluble portion of these carbons would result in precipitation of the iron and fouling of the carbon and could not be tolerated in this system. In addition, continuous treatment would soon result in the soluble portion of the carbon being removed. The resultant carbon would be of a different nature and react differently toward this process.

To alleviate this problem, it was decided to neutralize the basic portion of the carbon by an acid wash before use. This was done reluctantly since past experience (BCR Project No. 2040) had shown that the adsorption-oxidation effects from an acid-washed carbon can be quite different from those effects from a carbon which has not been acid washed. Thus, on the day prior to each test, the carbon to be used was immersed in deionized water containing 3 ml of 3N H_2SO_4. For each test, a fresh sample of carbon was used.

Since past tests (BCR Project 2040) had shown a first test with a fresh sample of carbon to be different from each of the succeeding ones, and that the second and succeeding ones gave similar results due to the elution of soluble material present in the carbon during the first test, two successive tests were performed with each carbon in both the batch and continuous flow series. In each case only the second test was evaluated, since equilibrium had probably been reached by that time and, therefore, this second test would be more representative of actual performance of that particular carbon.

Batch Tests -- The data representing the batch tests are summarized in Table 10. For ease of interpretation, the four separate variables are identified, with the high and low level of each variable being represented by + and - signs respectively.

The data in Table 10 were employed more fully in the calculation of main effects and variable interactions for each of the four responses. For this purpose, a codified design and calculation matrix, shown in Table 11, was used. The derivation of this matrix is described by Davies.(19) The positive or negative signs for variable interaction were obtained simply by algebraic multiplication for the signs of each single variable involved in the interaction. Main effects and interactions were calculated by multiplying the response values from Table 10 by the corresponding effect elements from Table 11, summing the results, and dividing by 8. The resulting value for single variables is also sometimes designated as an average effect, since, for two levels of the variable only, it is simply the difference between the average response to all tests conducted at the first level of the variable and that of all tests at the second level. If the effect of one variable changes at different levels of another variable, the two variables are said to interact. The relative importance of the variable or variables in question is reflected by the absolute magnitude of the calculated main effect or interaction. First-order (two variable) interactions are sometimes easy to interpret in terms of the physical behavior of the system. Second- and higher-order interactions are often less readily understood, and are often of minor significance in any case.

The main effects and interactions obtained in the manner described above are listed in Table 12. The calculations were less time-consuming since a computer program was employed. This enabled the evaluation of additional responses in this and in subsequent experiments. As stated before, only the second test of a series was evaluated since the results of these second tests are felt to be representative of the performance of the carbon after the soluble material present with the carbon has been removed.

As shown in Table 12, the main effects and interactions for each response are grouped according to the number of variables involved and are listed in order of decreasing absolute magnitude in each group. For the batch tests, the data indicated that the most significant variable affecting percent Fe^{2+} removed was Variable 4, concentration of Fe^{2+} in the original water. The negative sign for that main effect simply meant that the Fe^{2+} was removed more effectively at the lower level of Fe^{2+} concentration (100 mg/l in this test). This effect was particularly apparent when one compares the results of Test 1 through Test 8 with the results of Test 9 through Test 16 in Table 10 under the

TABLE 10. RESULTS OF STATISTICAL DESIGN I EXPERIMENT ON VARIABLES AFFECTING IRON REMOVAL. BATCH TESTS

	Variables*				Responses	
	1	2	3	4		
Test	Surface Area	Particle Size	Aeration Rate	Fe^{2+} Concentration	Fe^{2+} Removed, percent	Fe_T Removed, percent
1	-	-	-	-	81	77
2	+	-	-	-	89	86
3	-	+	-	-	62	61
4	+	+	-	-	64	59
5	-	-	+	-	82	75
6	+	-	+	-	94	93
7	-	+	+	-	74	70
8	+	+	+	-	82	75
9	-	-	-	+	25	18
10	+	-	-	+	33	30
11	-	+	-	+	19	20
12	+	+	-	+	17	18
13	-	-	+	+	74	60
14	+	-	+	+	40	36
15	-	+	+	+	39	34
16	+	+	+	+	30	25

*Variable Identification

Variable	Levels	
	+	-
Surface Area	950-1100 m^2/g	800 m^2/g
Particle Size	8 x 10 mesh	20 x 40 mesh
Aeration Rate	500 ml/min	50 ml/min
Fe^{2+} Concentration	1000 mg/l	100 mg/l

TABLE 11. CODIFIED DESIGN AND CALCULATION MATRIX

Test	Variable				Interactions										
	1	2	3	4	(1,2)	(1,3)	(1,4)	(2,3)	(2,4)	(3,4)	(1,2,3)	(2,3,4)	(1,2,4)	(1,3,4)	(1,2,3,4)
1	-	-	-	-	+	+	+	+	+	+	-	-	-	-	+
2	+	-	-	-	-	-	-	+	+	+	+	-	+	+	-
3	-	+	-	-	-	+	+	-	-	+	+	+	+	-	-
4	+	+	-	-	+	-	-	-	-	+	-	+	-	+	+
5	-	-	+	-	+	-	+	-	+	-	+	+	-	+	-
6	+	-	+	-	-	+	-	-	+	-	-	+	+	-	+
7	-	+	+	-	-	-	+	+	-	-	-	-	+	+	+
8	+	+	+	-	+	+	-	+	-	-	+	-	-	-	-
9	-	-	-	+	+	+	-	+	-	-	-	+	+	+	-
10	+	-	-	+	-	-	+	+	-	-	+	+	-	-	+
11	-	+	-	+	-	+	-	-	+	-	+	-	-	+	+
12	+	+	-	+	+	-	+	-	+	-	-	-	+	-	-
13	-	-	+	+	+	-	-	-	-	+	+	-	+	-	+
14	+	-	+	+	-	+	+	-	-	+	-	-	-	+	-
15	-	+	+	+	-	-	-	+	+	+	-	+	-	-	-
16	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

TABLE 12. MAIN EFFECTS AND INTERACTIONS BASED ON DATA FROM BATCH TESTS

	Responses			
	Fe^{2+} Removed, percent		Fe_T Removed, percent	
	Variable(s)	Main Effects and Interactions	Variable(s)	Main Effects and Interactions
Single Variable:	4	-43.88	4	-44.38
	2	-16.38	2	-14.12
	3	15.62	3	12.38
	1	- 0.88	1	0.88
Two Variable Interactions:	1,4	- 8.38	2,3	- 8.75
	3,4	6.62	1,4	- 6.62
	1,3	- 4.88	3,4	4.88
	1,2	0.62	1,3	- 3.38
	2,4	- 0.38	1,2	- 2.88
	2,3	0.12	2,4	2.38
Three Variable Interactions:	2,3,4	- 5.88	1,3,4	- 7.38
	1,2,3	4.62	2,3,4	- 5.88
	1,2,4	3.12	1,2,3	3.38
	1,3,4	- 0.74	1,2,4	3.12
Four Variable Interactions:	1,2,3,4	4.12	1,2,3,4	3.88

Designation of Variables:
1 = Surface area
2 = Particle size
3 = Aeration rate
4 = Fe^{2+} concentration

heading "Responses". With the single exception of Test 13, the percent Fe^{2+} removed was greater in Test 1 through Test 8, at the lower level of Fe^{2+} in the original water, than in Test 9 through Test 16, at the higher level of Fe^{2+} in the water. This indicated contact of the water (containing Fe^{2+}) -carbon mixture to be extremely important to removal of Fe^{2+}. The same can be said of the results with percent Fe_T removed. (See Table 10.)

Particle size and aeration rate affected both removal of Fe^{2+} and of total iron, Fe_T (which includes both Fe^{2+} and Fe^{3+}). The negative value for particle size (Table 12) indicated more effective iron removal at the lower level of that particular variable while the positive value for aeration rate indicated that a higher aeration rate was desirable. The absolute magnitude of both of these indicated the influence of particle size and aeration rate to be much less than that of Fe^{2+} concentration. Each, though, again implied that more efficient contact would have resulted in more effective iron removal.

Surface area did not seem to influence the results of the test since the magnitude of that particular main effect was less than 1. It should not be surprising that the relatively large iron molecule did not seem to be affected by a change in the number of relatively small micropores of the carbon as measured by surface area. There was no significant interaction between the variables, since the absolute magnitude of the first-order interactions from these tests did not even begin to approach the magnitude of the single variable main effects.

In summary of the batch tests, the concentration of Fe^{2+} in the synthetic coal mine water was the single most important variable. The most effective iron removal occurred at the lower concentrations of Fe^{2+}. Of lesser importance were particle size (finer particles for more effective iron removal) and aeration rate (higher rate for more effective removal). Surface area was not a significantly affecting variable nor was there significant interaction between variables. All results of the factorial experiment for the batch tests indicated that more efficient contact of the carbon-water system would have resulted in more effective iron removal.

Continuous Flow Tests -- As with the batch tests, continuous flow (column) tests were conducted with an identical factorial experiment and evaluated in the same manner. The data representing these continuous flow tests are summarized in Table 13. Again, two successive tests were conducted for each of the 16. For the reasons stated in the discussion of the batch tests, only the second test was evaluated. The data in Table 13 were again employed in the calculation of main effects and variable interactions for each of the 12 responses using the codified design and calculation matrix already presented in Table 11 and the procedure as already outlined.

TABLE 13. RESULTS OF STATISTICAL DESIGN I EXPERIMENT ON VARIABLES AFFECTING IRON REMOVAL. CONTINUOUS FLOW TESTS.

Test	Variables*				After 5 min		After 120 min		After 180 min	
	1	2	3	4	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T
	Surface Area	Particle Size	Aeration Rate	Fe^{2+} Concentration	Removed, percent	Removed, percent	Removed, percent	Removed, percent	Removed, percent	Removed, percent
1	-	-	-	-	68	62	16	5	17	10
2	+	-	-	-	82	80	61	43	64	41
3	-	+	-	-	27	16	18	4	21	6
4	+	+	-	-	34	23	11	5	11	9
5	-	-	+	-	55	48	45	4	2	13
6	+	-	+	-	25	26	45	43	61	43
7	-	+	+	-	11	14	14	9	17	12
8	+	+	+	-	32	22	15	6	17	12
9	-	-	-	+	45	36	22	16	18	11
10	+	-	-	+	74	68	23	16	28	10
11	-	+	-	+	6	5	15	5	15	5
12	+	+	-	+	22	14	10	5	8	5
13	-	-	+	+	62	55	37	12	39	20
14	+	-	+	+	80	70	38	18	40	12
15	-	+	+	+	32	25	5	9	2	9
16	+	+	+	+	16	12	12	9	10	6

* Variable Identification

Variable	Levels	
	+	-
Surface Area	950-1100 m^2/g	800 m^2/g
Particle Size	8 x 10 mesh	20 x 40 mesh
Aeration Rate	500 ml/min	50 ml/min
Fe^{2+} Concentration	1000 mg/1	100 mg/1

These main effects are listed in Table 14. The absolute magnitude of the values for the variable interactions were small; therefore, the interactions were judged to be insignificant and the values were not presented here. For these tests, the data indicated that the most significant variable affecting percent Fe^{2+} and Fe_T removed was Variable 2, particle size of the carbon. The negative sign for that main effect simply meant that iron was removed more effectively at the lower level of particle size (20 x 40 mesh in this experiment). It is doubtful whether this effect from particle size would have been particularly apparent had it not been for the calculation of this main effect as described. In any event, the absolute magnitude of this, the most significant variable, is only about one-half of the absolute magnitude of the most significant variable in the batch tests (Table 12) indicating a degree of importance for particle size in the continuous flow tests less than that for aeration rate, the most significant variable in the batch tests.

Variables 1 and 4 were similar in their effect on the continuous flow tests (except for the first 5 min of a test). The negative sign on Variable 4 simply meant that more effective iron removal occurred at the lower level of Fe^{2+} (100 mg/l in this experiment). The positive sign for Variable 1 simply meant that more effective iron removal occurred at the higher level of surface area (950-1100 m^2/g). In the evaluation of this test, it must be pointed out that there was, at times during the test, not much difference in the absolute magnitude of the main effects and that the relative importance of the variables changed as the test progressed.

It must also be pointed out that considerable difficulty was experienced in maintaining (a) a constant flow and (b) any flow at all during some of the 16 tests. In fact, these tests were completed only by (a) stopping the flow and aerating for 1 minute followed by (b) stopping the aeration and draining the tube for two minutes. This was necessary in Tests 2, 5, 6, 10, 13, and 14. Tests 5, 6, 13, and 14 involved the small particle size carbon and high aeration rate. Tests 2 and 10 also involved small particle size carbon but low aeration rate. The use of the carbon having high surface area in combination with the aforementioned conditions made this unusual procedure necessary. The particular set of conditions resulting in erratic or no flow through the column was not discovered until well into the tests for this factorial experiment. The experiment was completed but with reservations concerning the evaluation of the data. The similarity of the signs (positive or negative) on the variables from this experiment with those from the batch tests again indicated that more efficient contact should have resulted in more effective iron removal. In addition, the mechanical difficulties experienced served to indicate that the column used in these tests was not adequate. It had already been established that the same type of flow problems would not be experienced with a column of 3 in. diameter (as compared to the column of 1 in. diameter used for the tests reported here). A column having at least a 3 in. diameter was used in most of the tests after this experiment.

TABLE 14. MAIN EFFECTS BASED ON DATA FROM CONTINUOUS FLOW TESTS.

	Response			
	Fe^{2+} Removed, percent		Fe_T Removed, percent	
	Variable	Main Effects	Variable	Main Effects
	After 5 Minutes			
Single Variable:	2	-38.88	2	-39.25
	1	7.38	1	6.75
	3	- 5.62	3	- 4.00
	4	0.38	4	- 0.75
	After 120 Minutes			
Single Variable:	2	-23.38	2	-13.12
	4	- 7.88	1	10.12
	1	5.38	4	- 3.62
	3	4.38	3	1.38
	After 180 Minutes			
Single Variable:	2	-21.00	2	-12.00
	1	13.50	4	- 8.50
	4	- 6.25	1	6.50
	3	0.75	3	3.75

Designation of Variables:
1 = Surface Area
2 = Particle Size
3 = Aeration Rate
4 = Fe^{2+} Concentration

Statistical Design II

The second set of factorial experiments covered the effect of pH, and concentrations of aluminum, manganese, and sulfate in the synthetic coal mine water on removal of iron. Both batch and continuous flow tests were conducted. Each series consisted of 16 tests. For reasons discussed previously, only the second of two successive tests was evaluated.

Batch tests -- The data representing the batch tests are summarized in Table 15. For ease of interpretation, again the four separate variables are identified, with the high and low level of each variable being represented by + and - signs respectively. The procedure for evaluating this factorial experiment was identical to that described previously. The data from Table 15 were employed in the calculation of both main effects and variable interactions for the eight responses using the codified design and calculation matrix already presented in Table 11 and the procedure as already outlined. These main effects are listed in Table 16.

For these tests, the data indicated that the most significant variable affecting percent Fe^{2+} and Fe_T removed was Variable 1, the pH of the synthetic coal mine water. The positive sign for that main effect simply meant that the iron was removed more effectively at the higher level of pH (3.5 in this experiment). This effect was particularly apparent when one compares the results of the odd-numbered tests with the results of the even-numbered tests in Table 15. In almost all cases, the percent Fe^{2+} and Fe_T removed was greater in the even-numbered tests, at the higher level of pH in the water, than in the odd-numbered tests, at the lower level of pH in the water.

The magnitude of Variable 4 indicated that this variable also affected iron removal. The positive sign on this variable indicated that iron was removed more effectively at the higher concentration of this variable, concentration of sulfate in the synthetic coal mine water. From the batch tests, no other variable or interaction between variables was judged to have an effect on iron removal.

Continuous Flow Tests -- As with the batch tests, continuous flow tests were conducted with a 2^4 factorial experiment and evaluated in the same manner as before. The data representing these continuous flow tests are summarized in Table 17. Two successive tests of 6-hour duration each were conducted for each of the 16, and only the second test was evaluated for reasons already discussed. The data in Table 17 were again employed in the calculation of main effects and variable interactions for each of the 12 responses using the codified design and calculation matrix presented in Table 11 and the procedure as already outlined. These main effects are listed in Table 18. For these tests, the data indicated that the most significant variable affecting percent Fe^{2+} and Fe_T removed was Variable 1, the pH of the synthetic coal mine water. The positive sign for that main effect meant that iron was removed more

TABLE 15. RESULTS OF STATISTICAL DESIGN II EXPERIMENT ON VARIABLES AFFECTING IRON REMOVAL. BATCH TESTS.

	Variables*				After 5 min		After 30 min		After 60 min		After 120 min	
Test	1 pH	2 Al	3 Mn	4 SO_4^{2-}	Fe^{2+} Removed, percent	Fe_T Removed, percent	Fe^{2+} Removed, percent	Fe_T Removed, percent	Fe^{2+} Removed, percent	Fe_T Removed, percent	Fe^{2+} Removed, percent	Fe_T Removed, percent
1	-	-	-	-	26	0	26	0	26	0	26	0
2	+	-	-	-	39	24	53	48	70	64	89	86
3	-	+	-	-	21	2	20	0	16	2	18	2
4	+	+	-	-	15	13	31	30	50	49	78	71
5	-	-	+	-	0	0	8	0	17	2	25	4
6	+	-	+	-	24	19	52	51	72	70	94	91
7	-	+	+	-	8	0	5	0	8	0	15	4
8	+	+	+	-	21	16	34	33	57	55	85	82
9	-	-	-	+	16	2	20	2	35	7	53	12
10	+	-	-	+	28	27	56	51	76	73	95	92
11	-	+	-	+	14	3	14	3	25	3	36	5
12	+	+	-	+	28	20	51	43	73	67	91	89
13	-	-	+	+	20	2	27	2	31	5	48	10
14	+	-	+	+	24	20	53	48	77	75	96	93
15	-	+	+	+	26	2	32	2	43	10	57	12
16	+	+	+	+	27	20	36	33	61	58	90	85

* Variable Identification

	Levels	
Variable	+	-
pH	3.5	1.5
Aluminum	200 mg/1	50 mg/1
Manganese	100 mg/1	25 mg/1
Sulfate	8,000 mg/1	450 mg/1

TABLE 16. MAIN EFFECTS BASED ON DATA FROM BATCH TESTS

	Fe^{2+} Removed, percent		Fe_T Removed, percent	
	Variable	Main Effects	Variable	Main Effects
	After 5 Minutes			
Single Variable:	1	9.38	1	18.50
	3	-4.62	4	2.75
	4	3.62	2	-2.25
	2	-2.12	3	-1.50
	After 30 Minutes			
Single Variable:	1	26.75	1	41.00
	2	-9.00	2	-7.25
	4	7.50	4	2.75
	3	-3.00	3	-1.00
	After 60 Minutes			
Single Variable:	1	41.88	1	60.25
	4	13.12	4	7.00
	2	-8.88	2	-6.50
	3	-0.62	3	1.25
	After 120 Minutes			
Single Variable:	1	55.00	1	80.00
	4	17.00	4	7.25
	2	-7.00	2	-4.75
	3	3.00	3	3.00

Designation of Variables:
1 = pH
2 = Aluminum
3 = Manganese
4 = Sulfate

TABLE 17. RESULTS OF STATISTICAL DESIGN II EXPERIMENT ON VARIABLES AFFECTING IRON REMOVAL. CONTINUOUS FLOW TESTS.

	Variables*				After 5 min		After 60 min		After 120 min		After 180 min	
Test	1 pH	2 Al	3 Mn	4 SO_4^{2-}	Fe^{2+} Removed, percent	Fe_T Removed, percent	Fe^{2+} Removed, percent	Fe_T Removed, percent	Fe^{2+} Removed, percent	Fe_T Removed, percent	Fe^{2+} Removed, percent	Fe_T Removed, percent
1	-	-	-	-	95	66	14	0	13	4	6	1
2	+	-	-	-	100	100	76	62	55	45	48	40
3	-	+	-	-	100	75	10	0	18	0	16	1
4	+	+	-	-	99	91	72	68	62	53	60	52
5	-	-	+	-	74	38	20	0	12	0	15	4
6	+	-	+	-	100	100	71	56	58	43	50	43
7	-	+	+	-	66	35	9	5	13	0	8	0
8	+	+	+	-	78	67	28	17	25	18	21	19
9	-	-	-	+	81	48	16	1	21	0	19	6
10	+	-	-	+	100	91	92	83	91	76	80	70
11	-	+	-	+	61	49	10	9	19	4	19	2
12	+	+	-	+	84	85	75	70	85	70	85	72
13	-	-	+	+	100	77	41	16	16	7	19	4
14	+	-	+	+	100	100	97	83	88	87	79	72
15	-	+	+	+	95	54	24	7	38	4	28	6
16	+	+	+	+	86	78	68	55	67	66	71	62

* Variable Identification

Variable	Levels	
	+	-
pH	3.5	1.5
Aluminum	200 mg/1	50 mg/1
Manganese	100 mg/1	25 mg/1
Sulfate	8,000 mg/1	250 mg/1

TABLE 17. RESULTS OF STATISTICAL DESIGN II EXPERIMENT ON VARIABLES AFFECTING IRON REMOVAL. CONTINUOUS FLOW TESTS. (Continued)

	Variables*				After 240 min		After 300 min		After 360 min	
	1	2	3	4	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T
Test	pH	Al	Mn	SO_4^{2-}	Removed, percent	Removed, percent	Removed, percent	Removed, percent	Removed, percent	Removed, percent
1	-	-	-	-	4	3	13	4	6	4
2	+	-	-	-	46	35	33	32	30	0
3	-	+	-	-	10	1	0	0	2	3
4	+	+	-	-	58	51	64	57	58	56
5	-	-	+	-	12	5	10	4	6	0
6	+	-	+	-	40	44	50	44	48	44
7	-	+	+	-	0	0	0	0	0	7
8	+	+	+	-	21	19	20	19	25	24
9	-	-	-	+	9	4	7	4	11	4
10	+	-	-	+	78	70	80	68	76	70
11	-	+	-	+	9	4	14	1	14	2
12	+	+	-	+	84	76	84	76	82	76
13	-	-	+	+	10	5	23	4	25	5
14	+	-	+	+	73	65	73	66	69	65
15	-	+	+	+	21	4	15	2	12	6
16	+	+	+	+	72	68	74	70	68	64

* Variable Identification

	Levels	
Variable	+	-
pH	3.5	1.5
Aluminum	200 mg/l	50 mg/l
Manganese	100 mg/l	25 mg/l
Sulfate	8,000 mg/l	250 mg/l

TABLE 18. MAIN EFFECTS BASED ON DATA FROM CONTINUOUS FLOW TESTS

	Fe^{3+} Removed, percent		Fe$_T$ Removed, percent		Fe^{3+} Removed, percent		Fe$_T$ Removed, percent	
	Variable	Main Effects	Variable	Main Effects	Variable	Main Effects	Variable	Main Effects
	After 5 Minutes				After 60 Minutes			
Single Variable:	2	-10.13	1	33.75	1	54.38	1	57.00
	1	9.38	2	-10.75	2	-16.38	4	14.50
	3	-2.63	3	-7.00	4	15.38	2	-8.75
	4	-0.63	4	1.25	3	-0.88	3	-6.75
	After 120 Minutes				After 180 Minutes			
Single Variable:	1	47.63	1	54.88	1	45.50	1	50.75
	4	21.13	4	18.88	4	22.00	4	16.75
	3	-5.88	2	-5.88	3	-5.25	3	-4.25
	2	-3.38	3	-3.38	2	-1.00	2	-3.25
	After 240 Minutes				After 300 Minutes			
Single Variable:	1	49.63	1	50.25	1	49.50	1	51.63
	4	20.63	4	17.25	4	22.50	4	16.38
	3	-6.13	3	-4.25	3	-3.75	3	-4.13
	2	0.38	2	-1.00	2	-2.25	2	-0.13
	After 360 Minutes							
Single Variable:	1	47.50	1	46.00				
	4	22.75	4	19.25				
	3	-3.25	2	5.75				
	2	-1.25	3	0.00				

Designation of Variables:
1 = pH
2 = Aluminum
3 = Manganese
4 = Sulfate

effectively at the higher level of pH (3.5 in this experiment). The importance of this variable remained apparent throughout the duration of each 6-hour test as indicated by the relatively large value for that main effect (See Table 18).

Following approximately the first hour of the tests, the absolute magnitude of Variable 4, concentration of sulfate in the synthetic coal mine water, indicated that this variable influenced percent Fe^{2+} and Fe_T removed. The positive sign meant that more effective iron removal occurred at the higher level of sulfate concentration. A comparison of the magnitude of this effect and the magnitude of the pH effect from Table 18 indicated that pH had a much greater effect on iron removal than did sulfate concentration. In addition, after about an hour, interaction between Variable 1 and Variable 4, pH and sulfate concentration, respectively, was evident. From these continuous flow tests, no other variable or interaction between variables was judged to have an effect on iron removal.

In summary, both from the batch tests and continuous flow tests, the pH of the synthetic coal mine water was the most important variable affecting percent Fe^{2+} and Fe_T removed. Most effective iron removal was accomplished at the higher pH (3.5) in this experiment. This fact is consistent with oxidation as the mechanism for iron removal since the rate of oxidation of Fe^{2+} is known to be greater at the higher pH. A greater degree of adsorption at the higher pH, though, was also possible. Again, both from the batch and continuous flow tests, the concentration of sulfate in the synthetic coal mine water also affected percent Fe^{2+} and Fe_T removed. More effective iron removal was accomplished at the higher concentration of sulfate. This effect, though, was of lesser importance than the effect from pH as evidenced by the relative magnitude of Variables 1 and 4 from Table 18. The interaction between those two variables might be explained in a number of ways. The presence of (a) large amounts of sulfate and (b) the relatively high concentration of H^+ at the pH range of this experiment might have interacted to form the HSO_4^- species. The high concentration of sulfate, 8000 mg/l, might also have simply saturated the system, and, therefore, forced the iron out of the solution by precipitation onto the activated carbon resulting in more effective iron removal. More extensive precipitation would have occurred at higher pH.

An examination of the analyses for aluminum, manganese, and sulfate in the synthetic coal mine water prior to and after the tests showed that no significant removal of any of these three constituents was obtained with activated carbon.

Additional Statistical Design Tests

A series of continuous flow experiments was designed to fill in gaps in the data left by the Statistical Design I and II experiments.

Effect of pH -- Previous experiments had demonstrated more effective iron removal at pH 3.5 than at pH 1.5. Experiments were then conducted with synthetic coal mine waters containing approximately 250 mg/l of Fe^{2+} and pH values of 1.5, 2.0, 2.5, 3.0, and 3.5. The results are listed in Table 19. Only the results of the second of two tests at each pH level are presented for reasons discussed previously. The data from Table 19 on removal of Fe^{2+} were plotted in Figure 9. From these data, tests at low pH, 1.5 and 2.0, did not result in effective removal of Fe^{2+} for any reasonable period of time. In fact, at these pH values, a level of removal of 50 percent was achieved only for a very few minutes. At the higher pH values of 2.5, 3.0, and 3.5, a 50 percent level of removal was achieved for over 2 hours.

The data from Table 19 on removal of total iron, Fe_T, including both Fe^{2+} and Fe^{3+} are presented in Figure 10. As in the evaluation of Fe^{2+} removal, more effective removal of Fe_T occurred at the higher level of pH.

Effect of No Manganese -- Previous tests have demonstrated that a high or a low level of manganese in the synthetic coal mine water had no effect on removal of iron. This was carried one step further by conducting a test with no manganese in the synthetic mine water. The results of this test are presented in Table 20 and compared in the same table with the results of a past experiment from the Statistical Design II set (See Table 17, Test No. 12). The results of the two tests, as listed in Table 20, were judged to be similar, thus reenforcing the conclusion that the concentration of manganese in the water had no effect on iron removal. The data from Table 20 are compared in Figure 11. The differences in iron removal during this test with no manganese and during Test No. 12 were judged, from this figure, to be small.

Effect of No Aluminum -- Previous experiments have demonstrated that a high or low level of aluminum in the synthetic coal mine water had no effect on removal of iron. In a manner similar to the test with no manganese, a test was conducted with no aluminum in the synthetic coal mine water. The results of this test are presented in the first part of Table 21 and these data are also plotted in Figure 11. The results of the test with no aluminum were judged to be similar to the results of the standard test, Test No. 12, as described in Table 20 and Figure 11, reenforcing the conclusion that the concentration of aluminum in the water had no effect on iron removal.

Effect of No Aeration -- Previous experiments have demonstrated that a high rate of aeration favorably affects the removal of iron. A test was conducted in which the water-carbon mixture in the column was not aerated for the duration of the 6-hour test. The results are presented, also, in Table 21 and Figure 11. From the data, the effectiveness of iron removal was judged to have decreased drastically in comparison with the standard test, Test No. 12.

TABLE 19. EFFECT OF pH ON REMOVAL OF IRON

Time, min	Experiment No. 444-7 pH 1.5 Percent removed		Experiment No. 444-11 pH 2.0 Percent removed		Experiment No. 444-14 pH 2.5 Percent removed		Experiment No. 444-12 pH 3.0 Percent removed		Experiment No. 444-9 pH 3.5 Percent removed	
	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T
0	100	100	100	100	100	100	100	100	100	100
30	54	44	44	29	70	53	64	46	71	64
60	25	20	32	16	63	43	65	48	62	55
120	17	11	20	0	61	28	63	38	56	47
180	14	7	10	0	52	18	62	31	44	35
240	3	5	21	0	50	13	60	26	41	35
300	4	11	28	1	40	11	49	19	31	26

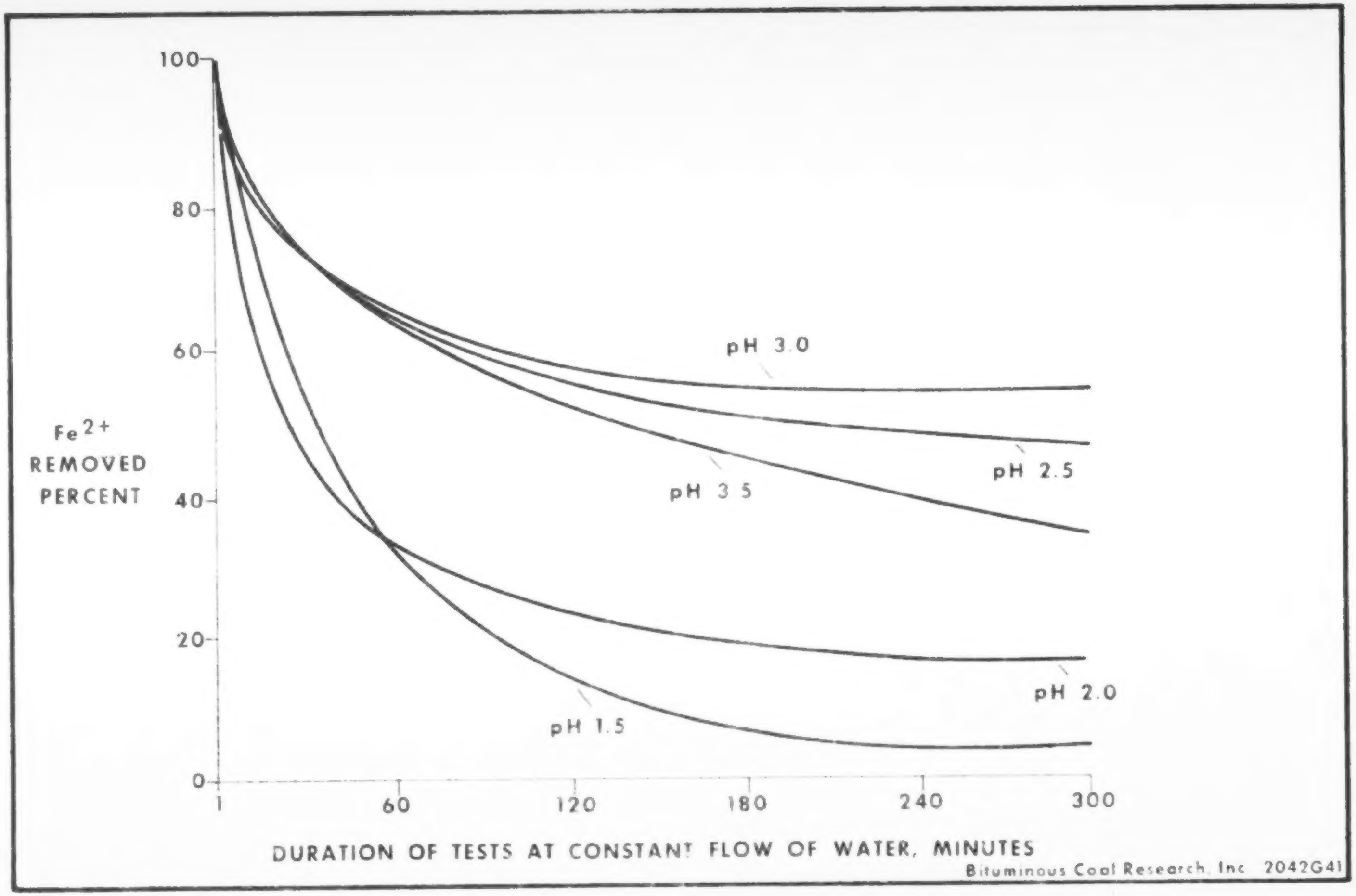

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Figure 9. Effect of pH on Removal of Fe^{2+}

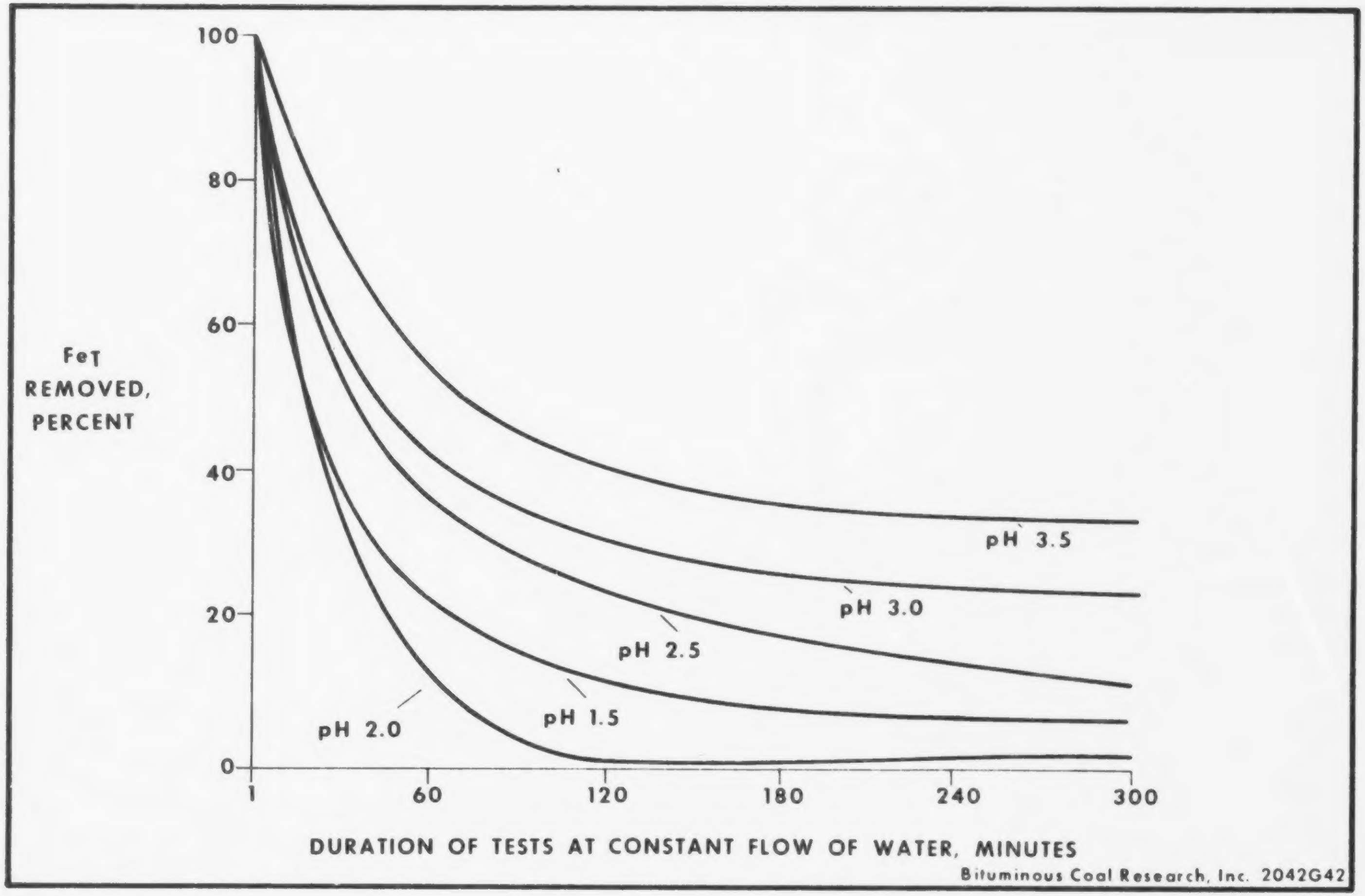

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Figure 10. Effect of pH on Removal of Fe_T

TABLE 20. EFFECT OF NO MANGANESE ON REMOVAL OF IRON

Time, min	Test with No Manganese Experiment No. 444-15					Standard Test for Comparison Experiment No. 443-81 (Test No. 12)				
		Fe^{2+}		Fe_T			Fe^{2+}		Fe_T	
	pH	mg/1	Percent removed	mg/1	Percent removed	pH	mg/1	Percent removed	mg/1	Percent removed
0	3.5	256	--	269	--	3.5	248	--	260	--
5	4.3	6	--	16	--	4.5	40	--	40	--
10	4.3	0	--	13	--	4.4	23	--	48	--
15	4.3	6	--	19	--	4.3	33	--	68	--
30	4.3	16	94	26	90	4.3	45	82	75	71
45	4.2	26	--	32	--	4.3	53	--	75	--
60	4.2	29	89	39	86	4.3	63	75	78	70
90	4.2	13	--	29	--	4.2	33	--	85	--
120	4.2	23	91	29	86	4.2	38	85	78	70
150	4.2	29	--	49	--	4.2	38	--	78	--
180	4.1	37	86	57	79	4.2	35	85	73	72
210	4.1	45	--	65	--	4.2	33	--	68	--
240	4.1	45	82	65	76	4.2	40	84	63	76
270	4.1	55	--	68	--	4.1	45	--	53	--
300	4.1	58	77	68	75	4.1	40	83	63	76
330	4.1	62	--	71	--	4.1	40	--	63	--
360	4.0	58	77	71	74	4.1	45	82	63	76

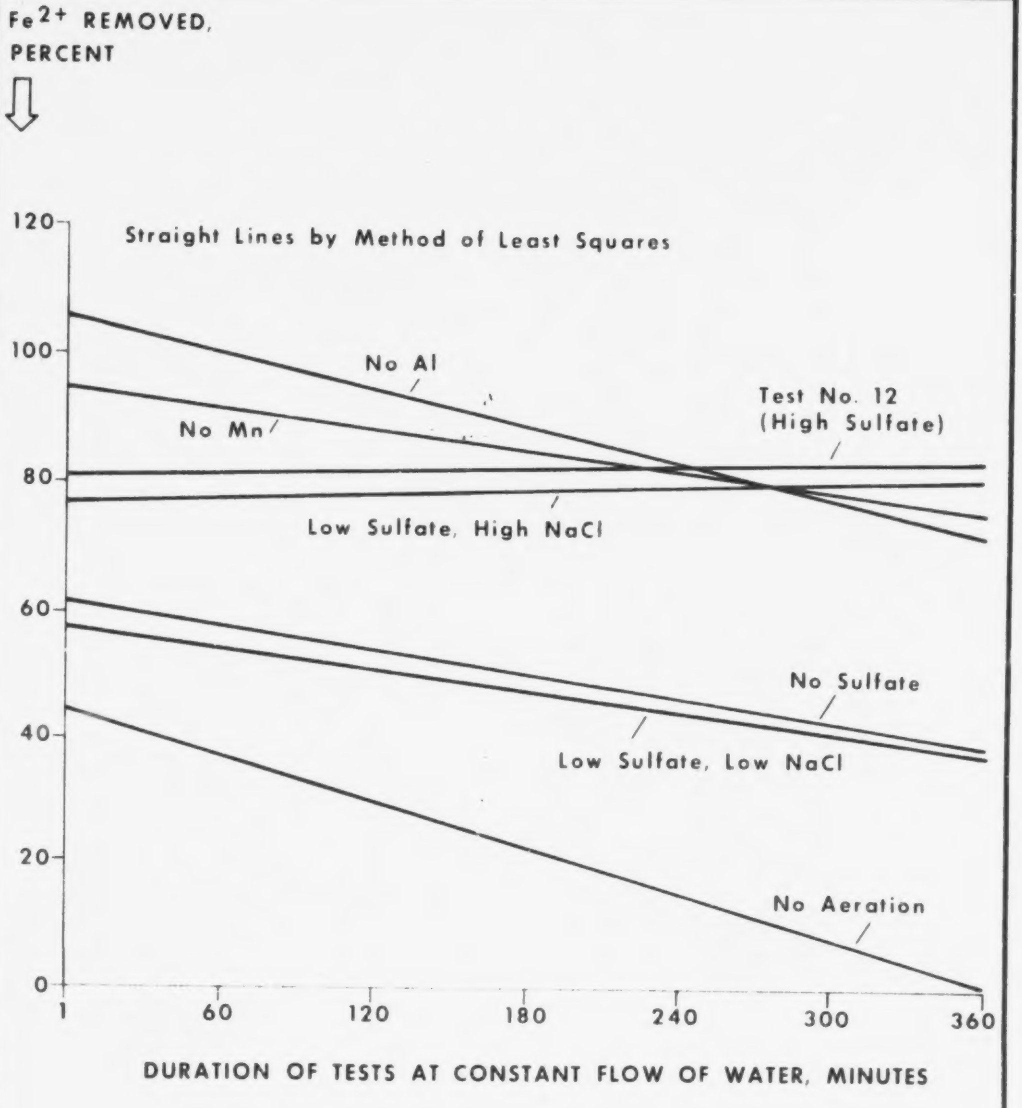

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Figure 11. Comparison of Effects of Various Process Variables on Removal of Iron

TABLE 21. EFFECT OF NO ALUMINUM AND NO AERATION ON REMOVAL OF IRON

Time, min	Test with No Aluminum Experiment No. 444-30					Test with No Aeration Experiment No. 444-22				
		Fe^{2+}		Fe_T			Fe^{2+}		Fe_T	
	pH	mg/1	Percent removed	mg/1	Percent removed	pH	mg/1	Percent removed	mg/1	Percent removed
0	3.5	244	--	263	--	3.5	273	--	286	--
5	6.5	0	--	0	--	4.7	62	--	88	--
10	6.4	0	--	0	--	4.7	71	--	97	--
15	6.4	0	--	0	--	4.6	68	--	97	--
30	6.2	0	100	0	100	4.5	107	61	123	57
45	6.3	0	--	0	--	4.4	175	--	188	--
60	5.9	0	100	0	100	4.4	205	25	211	26
90	5.4	0	--	0	--	4.4	227	--	240	--
120	4.9	0	100	6	98	4.3	224	18	237	17
150	4.8	13	--	25	--	4.3	218	--	250	--
180	4.8	26	89	32	88	4.3	224	18	256	10
210	4.7	31	--	37	--	4.2	221	--	256	--
240	4.6	36	85	42	84	4.2	218	20	256	10
270	4.6	55	--	62	--	4.2	227	--	244	--
300	4.5	62	75	68	74	4.2	250	8	256	10
330	4.5	65	--	75	--	4.2	263	--	266	--
360	4.5	68	72	81	69	4.2	256	6	276	3

Removal of iron by adsorption should not have required aeration, yet this test demonstrated aeration to be necessary. This is an additional indication that iron removal was accomplished by an oxidation mechanism in this process, or, at least, by a combination of oxidation and adsorption.

To further explore this aeration effect, continuous flow tests were also conducted according to the general procedure with actual coal mine water and with air, nitrogen, and oxygen, each at flow rates of 150 ml/min and with no air. The results of these tests are presented in Table 22 and the data concerning Fe^{2+} plotted in Figure 12. From these data, tests with nitrogen and no air resulted in ineffective removal of iron. As in past tests, aeration aided in removing iron more effectively. The most effective removal occurred in the test where oxygen was bubbled through the carbon-water mixture.

During this test and the test with nitrogen sparging, the dissolved oxygen content of the mine water was 4 to 6 mg/l, having decreased from an original value of 10 mg/l in the raw water; therefore, the improved effectiveness cannot be attributed to an increase in dissolved oxygen content of the water from the use of oxygen. The mechanism could involve adsorption of oxygen by the carbon and subsequent reaction by the diradical -O-O- thus formed (26) to extract electrons from the adsorbed ferrous ions.

Effect of No Sulfate -- Previous tests have indicated that a high concentration of sulfate favorably affects the removal of iron. A test was conducted in which sulfate was omitted from the synthetic coal mine water by adding the Fe^{2+} as ferrous chloride instead of as ferrous sulfate as was normally done. The results are presented in Table 23 and the data also plotted in Figure 11. Also included in Table 23 and Figure 11 are results of a test with low concentrations of both sulfate and NaCl and a test with a low concentration of sulfate and a high concentration of NaCl. The test with no sulfate present in the synthetic coal mine water resulted in significantly poorer iron removal as judged by comparison with data from the standard test, Test No. 12, in Table 20 and Figure 11. This seemed to reenforce the original conclusion that a high concentration of sulfate favorably affected iron removal.

At this point, there was concern on the part of the BCR investigators as to whether, in fact, sulfate itself was affecting iron removal. The concentration selected as the high level of sulfate for the Statistical Design II experiment was 8,000 mg/l since concentrations of sulfate of this level are not too uncommon in actual coal mine waters. But this was a higher concentration than that of any other species chosen for these tests. It was possible that the high total concentration of material in the water was resulting in a somewhat saturated solution and that this saturation was, itself, responsible for driving the iron out of solution. A test was planned, then, with a high concentration of ions other than sulfate.

TABLE 22. EFFECT OF AERATION, NO AERATION, NITROGEN SPARGING, AND OXYGEN SPARGING ON REMOVAL OF IRON

	Aeration Experiment No. 444-88					No Aeration Experiment No. 444-90				
		Fe^{2+}		Fe_T			Fe^{2+}		Fe_T	
Time, min	pH	mg/l	% Removed	mg/l	% Removed	pH	mg/l	% Removed	mg/l	% Removed
0	2.8	305	--	429	--	3.0	240	--	334	--
30	4.3	175	43	188	56	4.3	94	61	127	62
60	4.3	198	35	205	52	4.2	175	27	198	41
120	4.2	231	24	240	44	4.2	224	7	253	24
180	4.1	234	23	253	41	4.1	234	3	261	22
240	4.1	224	27	234	45	4.1	263	0	273	18
300	4.1	224	27	244	43	4.1	263	0	273	18
360	4.2	218	29	234	45	4.1	263	0	273	18

	Nitrogen Sparging Experiment No. 444-92					Oxygen Sparging Experiment No. 444-94				
		Fe^{2+}		Fe_T			Fe^{2+}		Fe_T	
Time, min	pH	mg/l	% Removed	mg/l	% Removed	pH	mg/l	% Removed	mg/l	% Removed
0	2.9	175	--	279	--	2.9	224	--	237	--
30	4.4	62	65	78	72	4.3	26	88	39	84
60	4.2	133	24	159	43	4.3	71	68	94	60
120	4.3	169	3	192	31	4.2	84	63	110	54
180	4.3	198	0	208	25	4.1	73	67	94	60
240	4.2	198	0	205	27	4.0	75	67	101	57
300	4.1	185	0	192	31	3.9	97	57	120	49
360	4.1	188	0	205	27	3.9	78	65	94	60

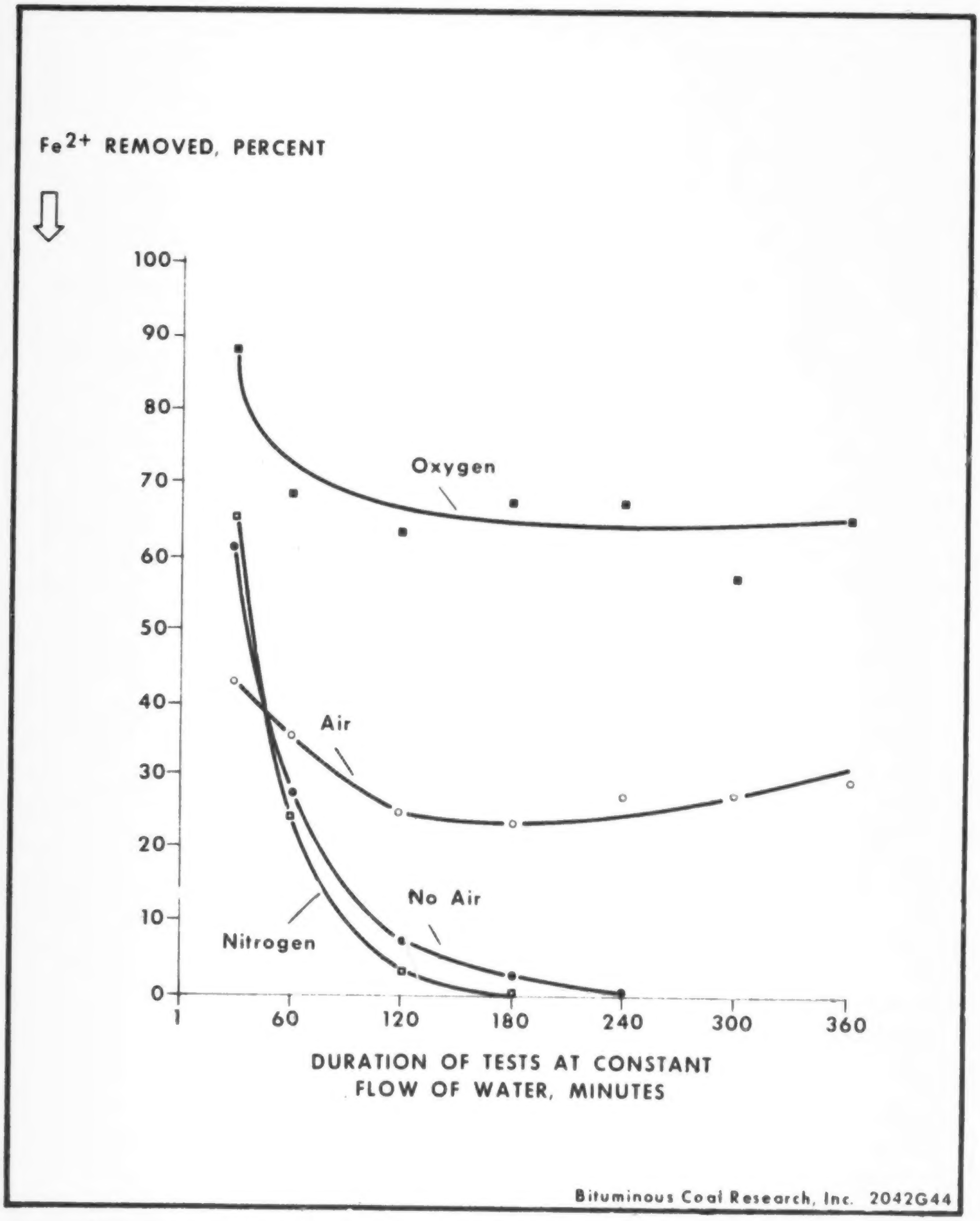

Figure 12. Effect of Aeration, No Aeration, Nitrogen, Sparging and Oxygen Sparging on Removal of Iron

TABLE 23. EFFECT OF NO SULFATE AND VARIOUS CONCENTRATIONS OF NaCl ON REMOVAL OF IRON

	Test with No Sulfate Experiment No. 444-36					Test with Low Sulfate, Low NaCl Experiment No. 444-40					Test with Low Sulfate, High NaCl Experiment No. 444-46				
		Fe^{2+}		Fe_T			Fe^{2+}		Fe_T			Fe^{2+}		Fe_T	
Time, min	pH	mg/l	Percent Removed	mg/l	Percent Removed	pH	mg/l	Percent Removed	mg/l	Percent Removed	pH	mg/l	Percent Removed	mg/l	Percent Removed
0	3.4	218	--	240	--	3.5	253	--	273	--	3.5	273	--	279	--
5	4.3	13	--	23	--	4.3	13	--	36	--	4.3	36	--	68	--
10	4.5	0	--	23	--	4.3	16	--	36	--	4.5	45	--	78	--
15	4.3	13	--	29	--	4.3	26	--	45	--	4.3	55	--	81	--
30	4.3	45	79	65	73	4.2	45	73	68	75	4.2	52	81	68	76
45	4.2	91	--	104	--	4.1	29	--	104	--	4.2	49	--	81	--
60	4.2	110	50	133	45	4.1	101	49	130	52	4.2	52	81	81	71
90	4.2	127	--	140	--	4.0	110	--	130	--	4.2	58	--	120	--
120	4.2	123	44	146	39	4.2	127	45	140	49	4.1	68	75	114	59
150	4.2	159	--	175	--	4.0	143	--	166	--	4.1	71	--	104	--
180	4.1	133	39	159	34	4.0	140	34	166	39	4.0	81	70	107	62
210	4.1	130	--	151	--	4.0	143	--	164	--	4.0	73	--	108	--
240	4.1	127	42	143	40	4.0	146	36	162	41	4.0	65	76	110	61
270	4.1	127	--	143	--	3.9	133	--	150	--	4.0	78	--	91	--
300	4.1	110	50	136	43	3.9	127	45	140	49	4.0	45	84	58	79
330	4.1	114	--	143	--	4.0	127	--	143	--	3.9	45	--	58	--
360	4.1	120	45	133	45	4.0	133	47	133	51	3.9	42	85	58	79

Sodium chloride, NaCl, seemed to be a logical choice as a replacement for (magnesium) sulfate. A test was first conducted with low concentrations of both NaCl and sulfate to observe any slight effect of NaCl on removal of iron. The results of this test are included in Table 23 and Figure 11. The effect of the aforementioned was judged to be similar to the effect when no sulfate was used for the test; in other words, the overall result was ineffective removal of iron. The NaCl itself did not seem to affect the iron removal.

For the test with a high level of NaCl, the concentration of NaCl was selected so that the overall concentration of ions, the total ionic strength, in the synthetic coal mine water would be equivalent to that of the water used in the standard test, Test No. 12. The results of this test are also presented in Table 23 and Figure 11. From the data, the results of this test were judged to be the same as the results of the standard test. Either a high concentration of sulfate or a similarly high concentration of NaCl resulted in effective removal of iron. What was observed was the effect of a high concentration of ions regardless of their nature, and not specifically the effect of sulfate concentration.

Effect of Bed Depth

The results of a series of tests with various amounts of carbon in the 19 in. x 3 in. column, resulting in different depths of the bed of carbon, are presented in Table 24. From the results in Table 24, the greater the depth of the bed of carbon, the more effective was the iron removal. This can be seen by a plot of the percent Fe^{2+} removed as shown in Figure 13, and a plot of the percent Fe_T removed as shown in Figure 14. A comparison of the time during which 50 percent of the iron was removed from each of these figures demonstrates this particular point.

That even 25 percent of the Fe^{2+} was not removed with the 3.5 cm-deep column can be seen from Figure 13. Again from Figure 13, the 9.2 cm deep column effected 50 percent iron removal for only a very short period of time. Using the time during which 50 percent of the Fe^{2+} is removed for each of the other three columns, 15.6, 21.9, and 27.9 cm deep, from Figure 13, the depth in centimeters necessary to achieve 50 percent removal for a time period of 1 minute was calculated to be 0.71, 0.72, and 0.72, respectively, for an average of 0.72 cm/min of 50 percent removal.

A similar calculation for total iron removal, Fe_T, from Figure 14 yields values of 0.72, 0.72, and 0.73, respectively, for the 15.6, 21.9, and 27.9 cm deep columns for an average for 0.72 cm/min of 50 percent removal of Fe_T.

Since the water used in these tests contained approximately 250 mg/l of iron and this water flowed through the column at a rate of 30 ml/min, the value of 0.72 cm/min was also calculated to be 0.72 cm/30 ml

TABLE 24. EFFECT OF BED DEPTH ON REMOVAL OF IRON

	80g Carbon 3.5cm Depth		260g Carbon 9.2cm Depth		440g Carbon 15.6cm Depth		620g Carbon 21.9cm Depth		800g Carbon 27.9cm Depth	
	Experiment Number 444-38		Experiment Number 444-37		Experiment Number 444-31		Experiment Number 444-27		Experiment Number 444-23	
	Percent removed		Percent removed		Percent removed		Percent removed		Percent removed	
Time, min	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{3+}	Fe_T
0	100	100	100	100	100	100	100	100	100	100
5	43	35	82	76	100	100	100	100	100	100
30	22	22	45	47	100	96	100	100	100	100
60	18	13	34	38	62	59	85	79	100	100
120	12	13	42	39	36	34	54	49	75	73
180	19	13	29	26	30	26	40	36	54	48
240	19	12	24	21	23	21	36	33	42	33
300	14	9	31	32	21	20	31	29	36	33
360	19	7	28	28	23	23	19	20	27	28

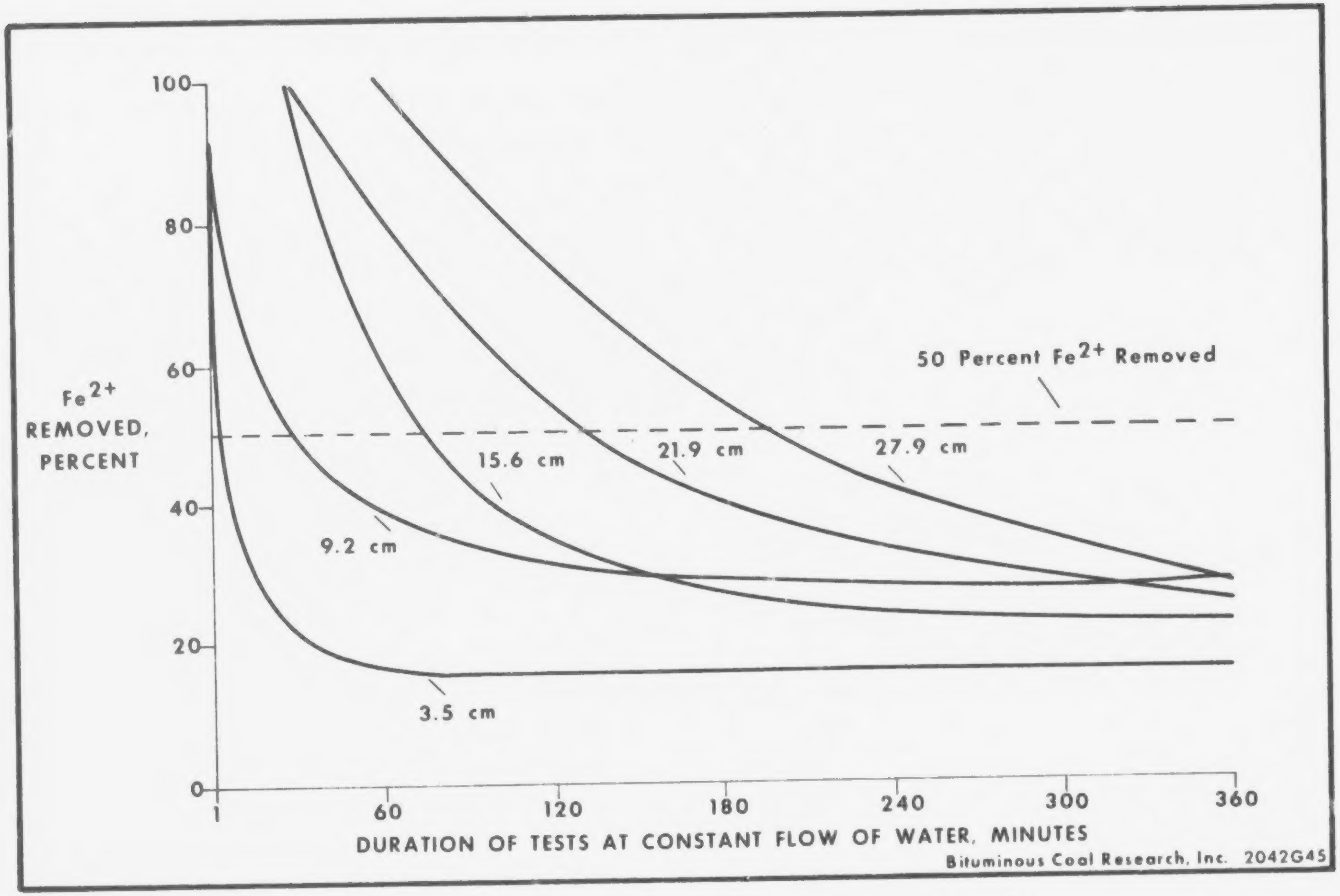

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Figure 13. Effect of Bed Depth on Removal of Fe^{2+}

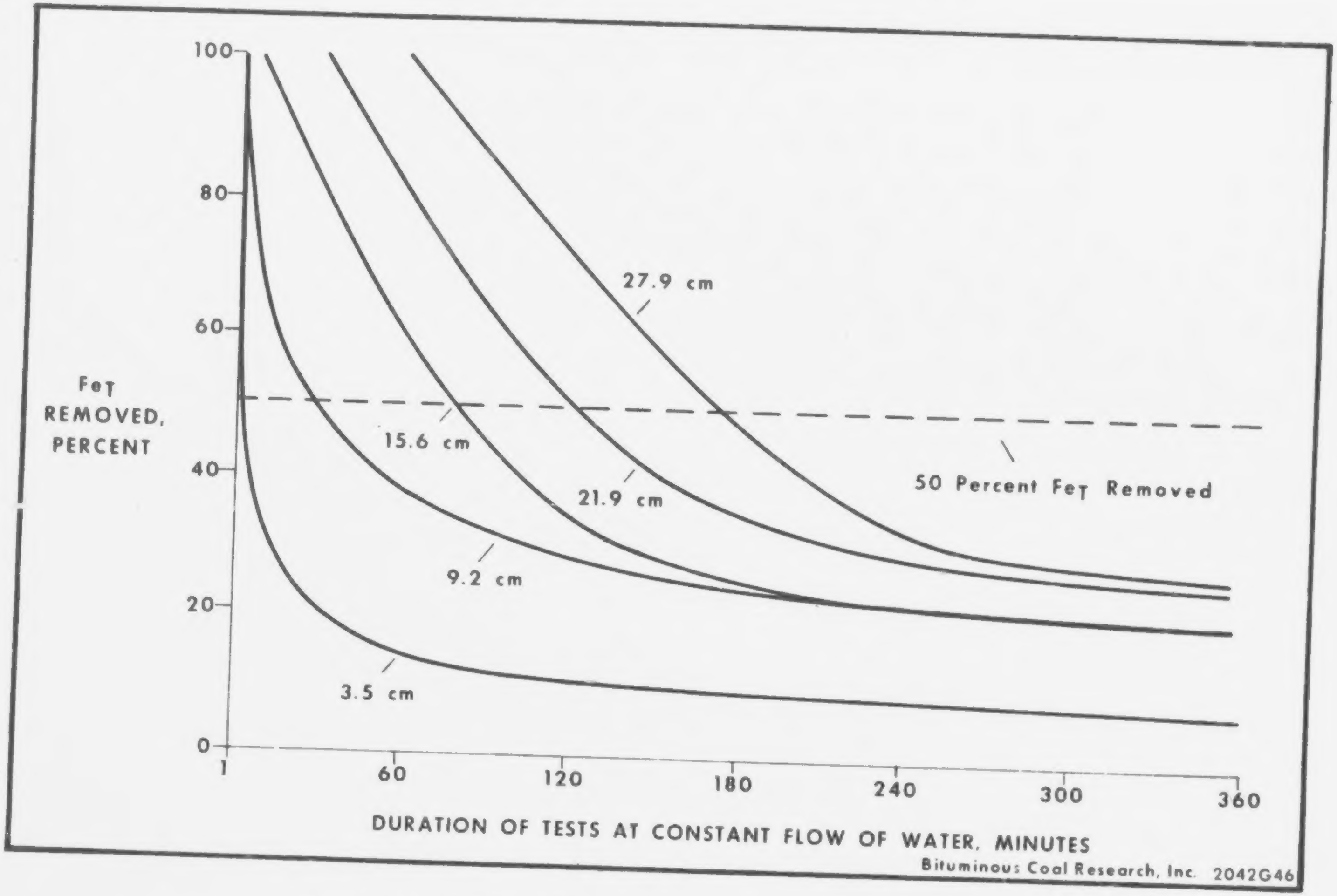

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Figure 14. Effect of Bed Depth on Removal of Fe$_T$

(0.024 cm/ml) or 0.72 cm/7.5 mg of iron (0.0096 cm/mg of iron) for 50 percent removal of iron.

Effect of Column Diameter

Three molded acrylic tubes of 3 in., 4 in., and 5 in., diameter were used in a series of tests, each with standard synthetic coal mine water and each with a separate 800 g sample of Nuchar WV-W carbon, to examine the effect of diameter of the column on iron removal. The results of these three tests are summarized in Table 25. Examination of the data in Table 25 reveals that the rate of removal of iron was similar regardless of the diameter of the column.

The same tubes were also used in similar tests with an actual coal mine water. The results of these tests are summarized in Table 26. The data showed little influence of column diameter on rates of removal of iron.

Effect of Temperature

Three continuous flow tests were conducted according to the general procedure and with standard synthetic coal mine water at temperatures of 12, 21, and 30C, to examine the effect of temperature on removal of iron. The results are summarized in Table 27, and the data plotted in Figures 15 and 16. The data showed little difference in iron removal between the tests at 12C and 21C, but a substantial difference in the test at 30C. More effective iron removal at the higher temperature can be seen from these figures.

Use of Materials Other Than Carbon

In the first test of this series, activated alumina was used in place of the carbon. The results of this test are presented in Table 28. The iron could be seen as a yellow precipitate on the top two inches of alumina in the column. The data in Table 28 also indicated ineffective iron removal, at least in this single test of relatively short duration.

In the second test of this series, charcoal briquettes were used in place of the carbon. The results of this test are presented in Table 29. The extremely effective removal of iron was attributed to the high pH resulting from the briquettes. An attempt was made after this test to lower the pH by passing 1N H_2SO_4 through the briquettes in the column. This only resulted in clogging the column, a fact which precluded the use of this material for the process.

The use of activated alumina and coal were examined in connection with bacteria and the results of these tests are described later in this report.

TABLE 25. EFFECT OF DIAMETER OF COLUMN ON REMOVAL OF IRON FROM SYNTHETIC COAL MINE WATER

	3 in. Diameter				4 in. Diameter				5 in. Diameter			
	Experiment No. 444-68				Experiment No. 444-57				Experiment No. 444-66			
	Fe^{2+}		Fe_T		Fe^{2+}		Fe_T		Fe^{2+}		Fe_T	
Time, min	mg/1	Percent removed	mg/1	Percent removed	mg/1	Percent removed	mg/1	Percent removed	mg/1	Percent removed	mg/1	Percent removed
0	268	-	276	-	253	-	263	-	263	-	292	-
30	0	100	0	100	0	100	16	94	0	100	0	100
60	45	83	62	78	32	87	58	78	13	95	36	88
120	68	75	127	54	97	62	136	48	78	70	117	60
180	120	55	136	51	127	50	136	48	133	49	169	42
240	169	37	192	30	133	47	156	41	146	44	188	36
300	153	43	172	38	153	40	179	32	179	32	185	37
360	175	35	192	30	172	32	188	29	195	26	208	29

TABLE 26. EFFECT OF COLUMN DIAMETER ON REMOVAL OF IRON FROM ACTUAL COAL MINE WATER

Time, min	pH	Fe^{2+} mg/l	Fe^{2+} Percent Removed	Fe_T mg/l	Fe_T Percent Removed
3 Inch Column 28 cm Carbon Depth Experiment No. 451-42					
0	3.0	240	--	334	--
30	4.3	107	55	127	62
60	4.2	123	49	143	57
120	4.2	156	35	179	46
180	4.1	162	33	182	46
240	4.1	172	28	188	44
300	4.0	192	20	211	37
360	4.0	192	20	208	38
4 Inch Column 18 cm Carbon Depth Experiment No. 451-44					
0	2.9	175	--	279	--
30	4.5	65	63	88	68
60	4.4	130	26	153	45
120	4.3	153	13	172	38
180	4.2	169	3	179	36
240	4.2	169	3	175	37
300	4.2	172	2	192	31
360	4.1	169	3	185	34
5 Inch Column 11 cm Carbon Depth Experiment No. 451-46					
0	2.9	224	--	347	--
30	4.3	166	26	211	39
60	4.3	166	26	195	44
120	4.3	175	22	205	41
180	4.2	185	17	211	39
240	4.2	192	14	221	36
300	4.2	221	1	240	31
360	4.1	237	0	240	31

TABLE 27. EFFECT OF TEMPERATURE ON REMOVAL OF IRON

	Low Temperature (12 C) Experiment No. 451-12				High Temperature (30 C) Experiment No. 451-15				Ambient Temperature (21 C) Experiment No. 451-10			
	Fe^{2+}		Fe_T		Fe^{2+}		Fe_T		Fe^{2+}		Fe_T	
Time, min	mg/1	Percent removed	mg/1	Percent removed	mg/1	Percent removed	mg/1	Percent removed	mg/1	Percent removed	mg/1	Percent removed
0	273	-	292	-	244	-	282	-	253	-	263	-
30	6	98	13	96	0	100	0	100	10	96	39	85
60	42	85	78	73	0	100	0	100	75	70	81	69
120	117	57	149	49	16	93	23	92	114	55	146	44
180	153	44	179	39	39	84	62	78	136	46	166	37
240	162	41	188	36	78	68	104	63	153	40	175	33
300	175	36	201	31	114	53	130	54	169	33	188	29
360	185	32	214	27	140	43	156	45	192	24	208	21

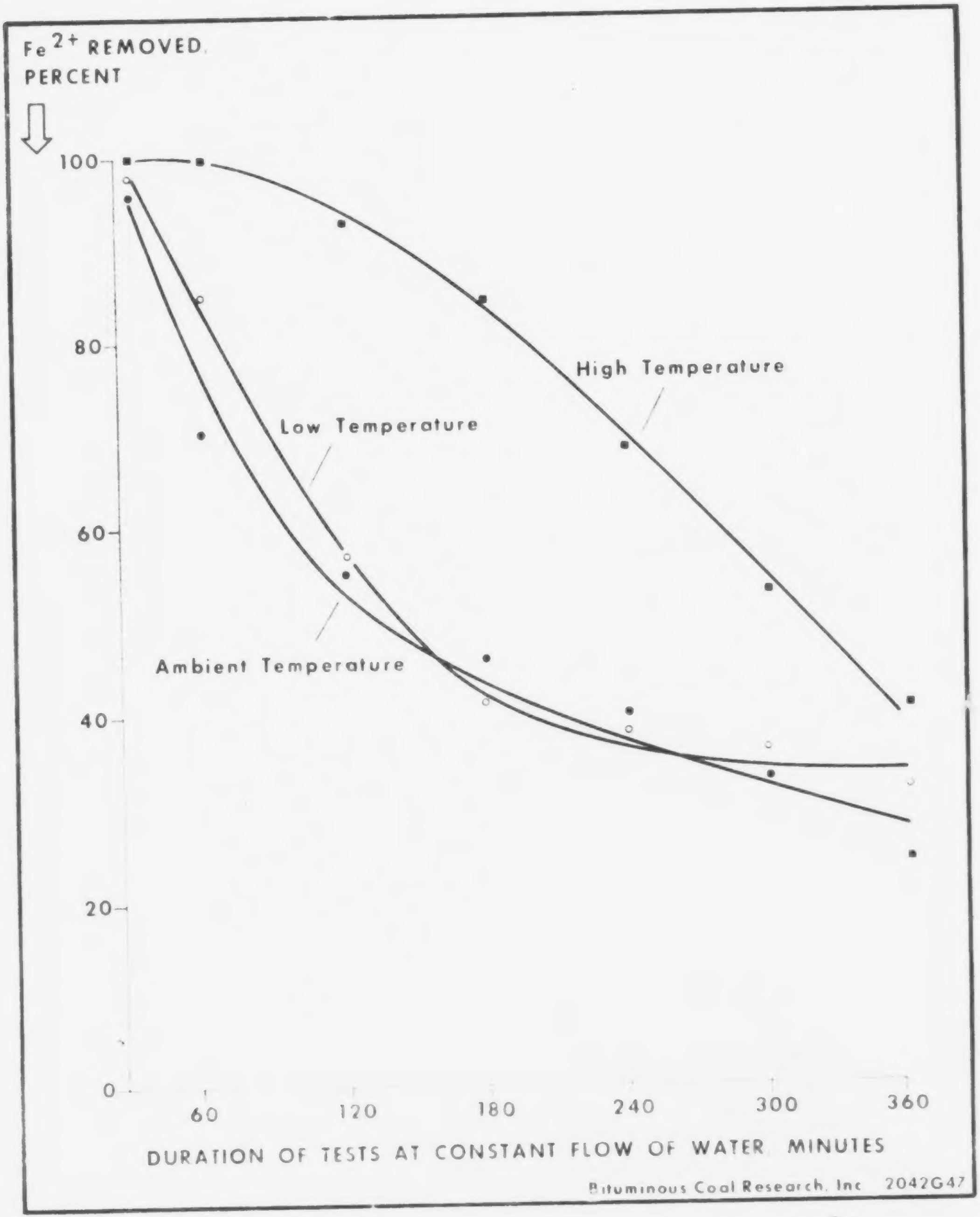

Figure 15. Effect of Temperature on Removal of Fe^{2+}

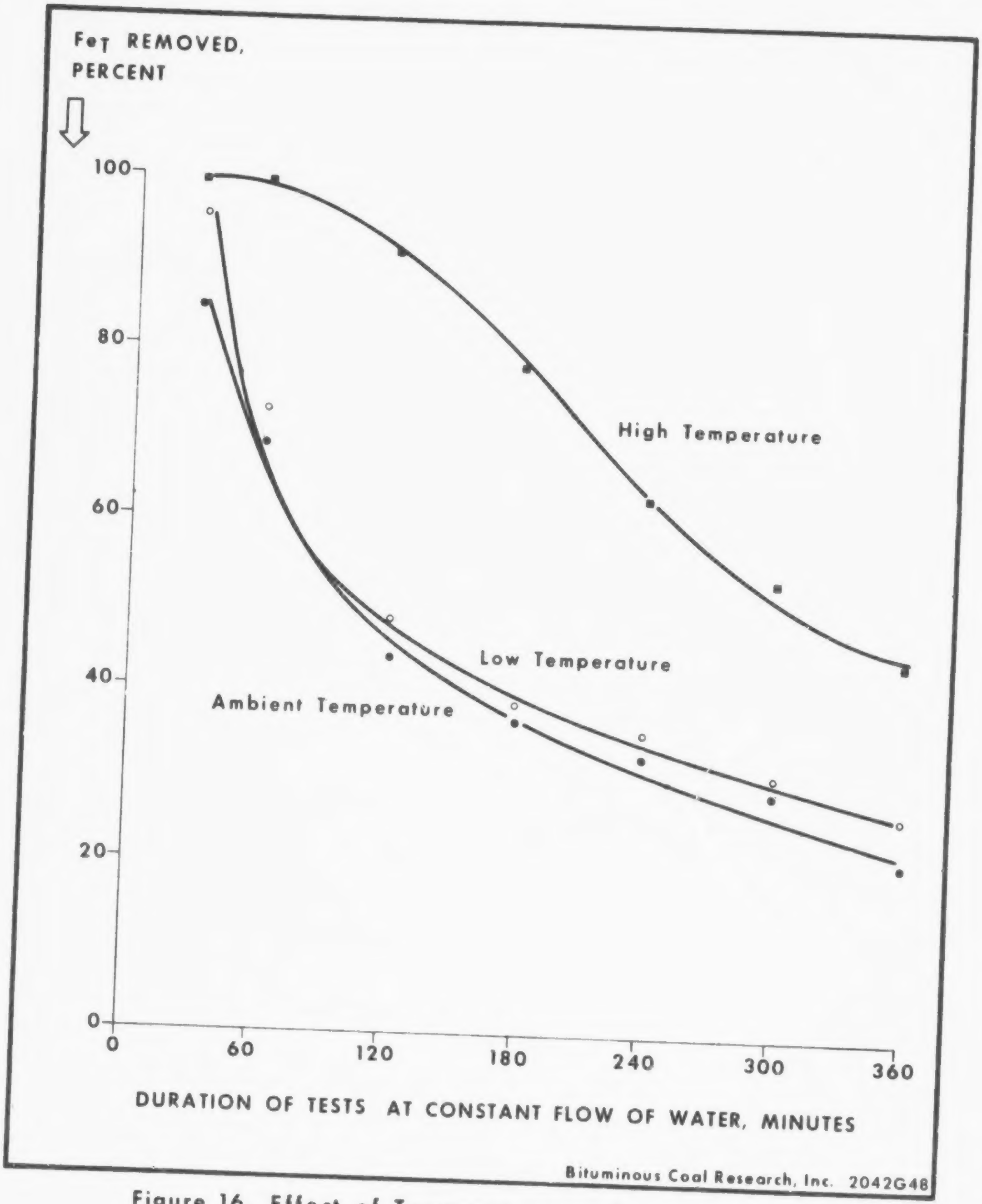

Figure 16. Effect of Temperature on Removal of Fe$_T$

TABLE 28. EFFECT OF ALUMINA ON REMOVAL OF IRON

Time, min	pH	Fe^{2+} mg/l	Fe^{2+} Percent removed	Fe_T mg/l	Fe_T Percent removed
0	3.0	256	--	289	--
5	4.4	133	48	179	38
10	4.4	185	28	198	31
15	4.4	198	23	221	24
30	4.4	198	23	221	24
45	4.4	192	25	201	30
60	4.4	198	23	221	24
90	4.4	192	25	201	30
120	4.4	185	28	198	31
150	4.4	192	25	198	31
180	4.4	182	29	198	31
210	4.4	182	29	192	34
240	4.4	175	32	185	36
270	4.4	166	35	175	39
300	4.4	169	34	175	39
330	4.4	166	35	175	39
360	4.4	167	35	175	39

TABLE 29. EFFECT OF CHARCOAL BRIQUETTES ON REMOVAL OF IRON

Time, min	pH	Fe^{2+} mg/l	Fe^{2+} Percent removed	Fe_T mg/l	Fe_T Percent removed
0	3.0	263	---	292	---
5	8.0	0	100	0	100
10	8.0	0	100	0	100
15	8.0	0	100	0	100
30	7.8	0	100	0	100
45	7.7	0	100	0	100
60	7.6	0	100	0	100
90	7.4	0	100	0	100
120	7.3	0	100	0	100
150	7.2	0	100	0	100
180	7.0	0	100	0	100
210	7.0	0	100	0	100
240	7.1	0	100	0	100
270	7.0	0	100	0	100
300	6.9	0	100	10	96
330	6.8	0	100	10	96
360	6.8	0	100	23	92

Tests with Actual Coal Mine Waters

Studies on this project with synthetic coal mine waters have demonstrated that the rate of removal of iron from the waters tested decreased drastically when the pH of that water was 2.5 or lower. When the pH of the water to be treated by this process is higher than 4.0 to 4.5, then significant precipitation of the iron compounds would occur, thereby blocking the activated sites on the carbon to further reaction and physically clogging the carbon column. Therefore, the coal mine waters containing Fe^{2+} which are most amenable to treatment by this process should have a pH between 2.5 and 4.0. In fact, coal mine waters having a pH below 2.5 are relatively rare, and those having a pH above 4.0 usually present little difficulty in treatment. Difficulties in treatment usually occur in those coal mine waters in the pH 2.5 to 4.0 range, and this process was designed to overcome some of the difficulties.

Two coal mine waters having the above characteristics desirable for this process were found and used in continuous flow tests. For the first series of tests, water was collected from the Tarrs discharge, which is near Tarrs, Westmoreland County, Pennsylvania and which has been used in past projects at BCR. In the past, the water typically contained 40 to 100 mg/l of iron as Fe^{2+}, an additional 50 to 80 mg/l of iron as Fe^{3+}, 50 to 100 mg/l of aluminum, and had a pH of approximately 3. As sampled for these tests, the water contained only 13 mg/l of Fe^{2+}, 45 mg/l of Fe_T, and had a pH of 3.0. Although the Fe^{2+} was considered lower than desired for these studies, this water was used in one test, stored overnight at a temperature of 1 C, and used the next day in a second test. The results are listed in Table 30. Throughout the duration of the first two tests, all iron was removed. The removal was more effective than with the synthetic coal mine water, but the low initial concentration of iron may have influenced the effective removal.

After the water had been stored at a temperature of 1 C for a weekend, iron ($FeSO_4$) was added to the water to increase the concentration of Fe^{2+} to the values shown in the last two columns in Table 30, and a third test was conducted with this water. The results of this test showed that a 50 percent level of iron removal, either Fe^{2+} or Fe_T, was attained throughout the duration of the 6-hour test. No further tests were conducted using this coal mine water.

For the second series of tests, water was collected at various points along a tributary of Little Plum Creek in Allegheny County, Pennsylvania, about five miles from BCR. The analyses of the first samples obtained at five locations along the stream are presented in Table 31. Since sampling points No. 3, 4, and 5 were progressively further downstream, they were more affected by weather conditions and by dilution from run-off. Tests were not conducted with water from points 4 and 5 both for this reason and because of difficulties in accessibility to the stream at these points.

TABLE 30. PRELIMINARY CONTINUOUS FLOW TESTS WITH TARRS COAL MINE WATER

	Experiment Number 444-42			Experiment Number 444-43			Experiment Number 444-47		
Time, min	pH	Fe^{2+} mg/1	Fe_T mg/1	pH	Fe^{2+} mg/1	Fe_T mg/1	pH	Fe^{2+} mg/1	Fe_T mg/1
0	3.0	13	45	3.0	13	45	3.1	266	347
5	6.9	0	0	6.2	0	0	4.6	0	0
10	7.2	0	0	6.4	0	0	4.4	0	0
15	7.5	0	0	6.3	0	0	4.4	0	0
30	7.9	0	0	6.0	0	0	4.5	0	0
45	7.8	0	0	5.2	0	0	4.5	0	0
60	7.5	0	0	4.8	0	0	4.5	0	13
90	7.4	0	0	4.6	0	0	4.3	55	84
120	7.4	0	0	4.6	0	0	4.2	68	104
150	7.2	0	0	4.5	0	0	4.1	114	133
180	7.1	0	0	4.5	0	0	4.0	120	136
210	7.0	0	0	4.6	0	0	4.0	130	143
240	6.7	0	0	4.8	0	0	4.2	127	149
270	5.3	0	0	4.4	0	0	4.0	136	153
300	5.0	0	0	4.5	0	0	4.0	133	159
330	--	--	--	4.4	0	0	4.0	136	159
360	--	--	--	4.3	0	0	3.9	143	159

TABLE 31. ANALYSES AT VARIOUS POINTS ALONG TRIBUTARY OF LITTLE PLUM CREEK

Sampling Point No.	pH	Fe^{2+} mg/l	Fe_T mg/l	Dissolved Oxygen, mg/l
1	3.0	390	516	8.5
2	3.4	117	153	9.1
3	3.3	156	198	11.6
4	3.4	107	123	12.0
5	4.6	62	71	11.5

Continuous flow tests were conducted according to the general procedure with water from sampling points 1, 2, and 3. The results of three tests each with these waters are presented in Tables 32, 33, and 34. Under the conditions specified by the general procedure, satisfactory removal of either Fe^{2+} or Fe_T was not achieved from the water containing relatively high concentrations of iron from sampling point No. 1, as indicated by the data in Table 32. A 50 percent level of iron removal was attained only for a very short duration of time during these tests. Similarly, the data from tests with water from sampling point No. 2, Table 33, show that a 50 percent or greater level of iron removal for any significant time was attained only in the first of the three tests. In fact, the results of the last of the three tests shown in Table 33, indicated elution of some of the iron which had been adsorbed and/or oxidized during the first two tests with this water. For these tests, a fresh sample of carbon was used for the waters from each sampling point and that carbon was then used for all three tests with the same water.

The results in Table 34 of tests with water from sampling point No. 3 in the last experiment of this series, indicate effective removal throughout the duration of the three tests and even slightly improved results with each of the three succeeding tests. The more effective removal of iron from water at sampling point No. 3, which is farther downstream, could be attributed to the dissolved oxygen content of the water, since this water had a concentration of 11.6 mg/l as compared to 8.5 mg/l for water from sampling point No. 1 and 9.1 mg/l for water from sampling point No. 2 (See Table 31). In addition, each water also contained a different initial concentration of iron.

Effect of Bacteria

Active cultures of Thiobacillus ferrooxidans, iron-oxidizing bacteria, and Thiobacillus thiooxidans, sulfur-oxidizing bacteria, were obtained from Indiana University of Pennsylvania at the 48-hour period of growth, the time at which they were said to be at the peak of their activity (27). Standard synthetic coal mine water was inoculated with the suspension of Thiobacillus ferrooxidans in a 10/1 ratio of water/suspension. A 500 ml portion of the inoculated synthetic coal mine water was aerated and the sample analyzed for Fe^{2+} and Fe_T to indicate any activity the bacteria might have. There was no change in Fe_T with time, but the Fe^{2+} content was reduced from the original 227 mg/l to: 191 mg/l in 1 hour; 161 mg/l in 2 hours; 9 mg/l in 24 hours. The conversion of Fe^{2+} to Fe^{3+} in the first hour, therefore, was 36 mg/l, in the second hour, 30 mg/l, and decreased gradually per hour every hour thereafter. This conversion corresponds favorably to that of Consolidation Coal Company's conversion using Ferrobacillus ferrooxidans in their Levi Moor micro-bio oxidation treatment plant reported to be up to 40 ppm/hour (28).

TABLE 32. RESULTS OF PRELIMINARY CONTINUOUS FLOW TESTS WITH TRIBUTARY OF LITTLE PLUM CREEK. SAMPLING POINT NO. 1.

	Experiment No. 451-34					Experiment No. 451-35					Experiment No. 451-36				
		Fe^{2+}		Fe_T			Fe^{2+}		Fe_T			Fe^{2+}		Fe_T	
Time, min	pH	mg/1	Percent removed	mg/1	Percent removed	pH	mg/1	Percent removed	mg/1	Percent removed	pH	mg/1	Percent removed	mg/1	Percent removed
0	2.9	279	--	403	--	2.8	289	--	403	--	2.9	276	--	377	--
30	7.0	0	100	0	100	4.3	71	75	91	77	4.2	104	62	130	66
60	6.6	0	100	10	98	4.3	175	39	205	49	4.2	169	39	192	49
120	4.9	91	67	114	72	4.2	231	20	253	37	4.1	198	28	227	40
180	4.8	172	38	201	50	4.2	263	9	286	29	4.2	229	17	248	34
240	4.4	188	33	211	48	4.2	263	9	289	28	4.1	244	12	276	27
300	4.3	192	31	224	44	4.2	276	4	295	27	4.0	256	7	273	28
360	4.3	214	23	240	40	4.1	286	1	299	26	4.0	273	1	276	27

TABLE 33. RESULTS OF PRELIMINARY CONTINUOUS FLOW TESTS WITH TRIBUTARY OF LITTLE PLUM CREEK. SAMPLING POINT NO. 2.

	Experiment No. 451-21					Experiment No. 451-26					Experiment No. 451-27				
		Fe^{2+}		Fe_T			Fe^{2+}		Fe_T			Fe^{2+}		Fe_T	
Time, min	pH	mg/1	Percent removed	mg/1	Percent removed	pH	mg/1	Percent removed	mg/1	Percent removed	pH	mg/1	Percent removed	mg/1	Percent removed
0	3.4	117	--	153	--	3.0	114	--	282	--	2.9	123	--	383	--
30	8.1	0	100	0	100	4.6	13	89	42	85	4.2	55	55	78	80
60	7.9	0	100	0	100	4.3	32	72	91	68	4.2	107	13	123	68
120	7.5	0	100	0	100	4.3	91	20	120	57	4.1	166	0	179	53
180	5.3	0	100	0	100	4.3	99	13	134	52	4.0	178	0	204	47
240	4.6	3	97	29	81	4.2	101	11	133	53	4.0	192	0	218	43
300	4.5	3	97	23	85	4.1	101	11	133	53	4.0	208	0	224	42
360	4.4	3	97	19	88	4.1	101	11	129	54	3.6	214	0	231	40

TABLE 34. RESULTS OF PRELIMINARY CONTINUOUS FLOW TESTS WITH TRIBUTARY OF LITTLE PLUM CREEK. SAMPLING POINT NO. 3.

	Experiment No. 444-84					Experiment No. 444-85					Experiment No. 444-86				
		Fe^{2+}		Fe_T			Fe^{2+}		Fe_T			Fe^{2+}		Fe_T	
Time, min	pH	mg/1	Percent removed	mg/1	Percent removed	pH	mg/1	Percent removed	mg/1	Percent removed	pH	mg/1	Percent removed	mg/1	Percent removed
0	3.0	55	--	198	--	3.2	62	--	192	--	3.4	55	--	97	--
30	7.8	0	100	0	100	4.5	0	100	0	100	4.3	0	100	0	100
60	7.0	0	100	0	100	4.3	0	100	0	100	4.3	0	100	0	100
120	5.0	0	100	10	95	4.3	3	95	23	88	4.2	0	100	0	100
180	4.8	13	76	32	84	4.2	0	100	23	88	4.2	0	100	0	100
240	4.5	26	53	39	80	4.2	6	90	29	85	4.2	0	100	0	100
300	4.4	23	58	42	79	4.1	3	95	23	88	4.2	0	100	0	100
360	4.3	29	47	68	66	4.1	6	90	23	88	4.1	0	100	0	100

Synthetic coal mine water which had not been inoculated was subjected to the same treatment, which resulted in no measurable change in Fe^{2+} even after having been aerated for 7 days. In neither experiment was carbon present. The bacteria were alive and active during these tests.

Tests with Bacteria-inoculated Water

Batch tests and continuous flow tests were conducted with synthetic coal mine water and Nuchar WV-W carbon, 12 x 40 mesh, according to the general procedure. These "standard" tests were compared with tests with synthetic coal mine water which had been inoculated with Thiobacillus ferrooxidans and/or Thiobacillus thiooxidans.

Batch tests -- Active cultures of Thiobacillus ferrooxidans were obtained from Indiana University of Pennsylvania in Silverman and Lundgren 9K basal salts + ferrous sulfate as the energy source. As received, the culture media contained 41 mg/l of Fe^{2+}, 610 mg/l of Fe_T, and had a pH of 1.9 by our analyses. A 10:1 mixture of synthetic to culture media was prepared and used in these batch tests and the continuous flow tests. The results of a "standard" batch test, with no bacteria present, and a test with Thiobacillus ferrooxidans are compared in Table 35.

It is apparent from the data in Table 35 that, in spite of the presence of iron oxidizing bacteria and aeration, the Fe^{2+} present with the culture as an energy source for the bacteria had been reduced to the Fe^{2+} state. Two samples of water from these two tests were analyzed for bacteria. No bacteria were found, indicating rather complete adsorption of the bacteria on to the activated carbon.

Another test was conducted with the synthetic coal mine water which had been inoculated with Thiobacillus thiooxidans. The results of this test are also presented in Table 35. This particular culture, by itself, was not expected to and, in fact, did not affect iron removal. It was desirable, though, to determine the effect of this culture on the process before combining it with the iron-oxidizing bacteria. The combination of iron-oxidizing and sulfur-oxidizing bacteria was said to accomplish oxidation of iron at a faster rate than if only the iron-oxidizing bacteria were present.

Finally, a test was conducted with the combination of iron-oxidizing and sulfur-oxidizing bacteria in the synthetic coal mine water. One liter of each culture was added to 10 liters of synthetic. The results are also presented in Table 35. As in the past tests with Thiobacillus ferrooxidans, the presence of bacteria did not enhance the oxidation of Fe^{2+} and, in fact, again resulted in reduction of the Fe^{3+} to the Fe^{2+} state.

TABLE 35. BATCH TESTS WITH BACTERIA-INOCULATED WATER

Time, min	"Standard" Test-No Bacteria Experiment No. 440-26		Thiobacillus ferrooxidans Added Experiment No. 433-48	
	Fe^{2+}, mg/l	Fe_T, mg/l	Fe^{2+}, mg/l	Fe_T, mg/l
0	245	248	227	615
5	208	215	411	595
10	195	199	407	575
15	175	178	401	555
30	158	166	397	455
45	109	130	345	390
60	76	93	324	375

Time, min	Thiobacillus thiooxidans Added Experiment No. 440-25		Thiobacillus ferrooxidans and Thiobacillus thiooxidans Added Experiment No. 440-27	
	Fe^{2+}, mg/l	Fe_T, mg/l	Fe^{2+}, mg/l	Fe_T, mg/l
0	219	231	188	560
5	223	233	337	540
10	212	226	331	520
15	199	225	333	540
30	175	193	310	510
45	163	180	247	500
60	159	177	272	530

Continuous Flow Tests -- As in the case of the batch tests, a "standard" continuous flow test with no bacteria in the synthetic coal mine water was conducted. The results of this test are compared in Table 36 with the results of a test with synthetic containing Thiobacillus ferrooxidans and also with the results of a test with synthetic containing a combination of Thiobacillus ferrooxidans and Thiobacillus thiooxidans. Again, as in the batch tests, reduction of iron back to the Fe^{2+} state was seen in the results of tests with bacteria present.

A further difficulty was experienced in the test with the combination iron-oxidizing and sulfur-oxidizing bacteria. The cultures, as received, contained iron as an energy source for the bacteria. This iron had been converted to the Fe^{3+} state by the bacteria during their growth period. The precipitated ferric iron caused the column to be blocked at 150 minutes into this test. Flow could then be maintained only by eliminating the aeration. Flow was continued for an additional 60 minutes with no aeration, for a total of 210 minutes.

In summary, the results of neither the batch nor the continuous flow tests have demonstrated effective removal of iron from synthetic coal mine water which had been inoculated with bacteria. In addition, reduction of iron from the Fe^{3+} back to the Fe^{2+} state occurred under these conditions, and this is undesirable to this process.

Tests with Bacteria-inoculated Carbon

Based on results of tests with bacteria, described above, the time element in oxidation of ferrous iron with carbon-bacteria systems was considered by conducting tests at least two weeks after suspensions of bacteria had been mixed with carbon. Both batch tests and continuous flow tests were conducted with standard synthetic coal mine water and Nuchar WV-W carbon, 12 x 40 mesh, which had been inoculated with iron-oxidizing bacteria, Thiobacillus ferrooxidans, 18 days before these tests so that the bacteria could first adapt to the new environment before being called upon to oxidize the iron. The bacteria were obtained from Indiana University of Pennsylvania and were the same as used in previous tests.

Batch Tests -- The results of "standard" batch tests with no bacteria were compared with the results of tests with the bacteria-inoculated carbon. The results of the "standard" batch tests are presented in Table 37. Two tests of 120 minute duration each were conducted with the no-bacteria system and two, also of 120 minute duration, with the bacteria-carbon system. The results of these are also shown in Table 37. From these data, it is apparent that iron removal was not enhanced by the presence of bacteria and that there was no evidence of the reduction of iron back to the Fe^{3+} state as in some past tests with bacteria.

TABLE 36. CONTINUOUS FLOW TESTS WITH BACTERIA-INOCULATED WATER

Time, min	"Standard" Test-No Bacteria Experiment No. 443-5		Thiobacillus ferrooxidans Added Experiment No. 433-49		Thiobacillus ferrooxidans and Thiobacillus thiooxidans Added Experiment No. 443-7	
	Fe^{3+}, mg/l	Fe_T, mg/l	Fe^{3+}, mg/l	Fe_T, mg/l	Fe^{3+}, mg/l	Fe_T, mg/l
0	235	240	228	590	188	560
5	28	39	166	-	182	184
10	28	29	326	338	208	266
15	38	39	401	-	220	292
30	133	150	328	483	278	525
60	156	173	197	588	170	500
90	170	175	184	588	163	540
120	176	182	169	584	150	585
150	182	190	157	590	138*	575*
180	190	196	153	660	120*	565*

* Stopped aeration but maintained flow

TABLE 37. BATCH TESTS WITH BACTERIA-INOCULATED CARBON

	"Standard" Tests - No Bacteria				Bacteria Added			
	First Test Experiment No. 440-32		Second Test Experiment No. 440-35		First Test Experiment No. 440-34		Second Test Experiment No. 440-36	
Time, min	Fe^{2+}, mg/1	Fe_T, mg/1	Fe^{2+}, mg/1	Fe_T, mg/1	Fe^{2+}, mg/1	Fe_T, mg/1	Fe^{2+}, mg/1	Fe_T, mg/1
0	251	259	251	259	251	259	251	259
5	15	73	10	65	58	670	30	580
10	7	45	6	47	45	634	21	570
15	2	30	2	37	25	395	19	570
30	1	17	1	25	24	370	15	570
45	1	14	1	18	20	360	11	570
60	1	12	1	17	20	320	11	540
90	1	11	1	13	14	250	11	505
120	1	8	1	11	12	205	11	500

Continuous Flow Tests -- The results of the test with bacteria-inoculated carbon and the 22 in. x 1 in. column are presented in Table 38 and compared in the same table with the results of a past "standard" test and a past test with bacteria which was added to the water, and not to the carbon. In this test, the carbon in the column had been inoculated with the bacteria 18 days prior to the test and growth of the bacteria was encouraged while they were given time to adapt to their new environment.

From the data in Table 38, there is no evidence of the reduction of Fe^{3+} during the test with the inoculated carbon, in contrast to the reduction evident during the test with the inoculated water. In the test with the inoculated carbon, there was specific evidence of a substantial amount of oxidation since (a) greater than 50 percent of the Fe^{2+} was removed throughout the 6-hour duration of the test, and (b) during this 6-hour period, there was a substantial difference between the Fe_T analyses and the Fe^{2+} analyses at any single point in time. This was the first evidence from this project of any substantial enhancement of iron removal with iron-oxidizing bacteria.

To examine the long term effects of the iron-oxidizing bacteria-activated carbon combination, continuous flow tests were conducted according to the general procedure with the carbon which had been inoculated with Thiobacillus ferrooxidans two months prior to these tests. Analysis of the water drained from the carbon prior to the tests did not show the presence of the bacteria. This did not necessarily indicate that the bacteria had not survived; those which survived could cling tenaciously to the carbon. The results of these tests are presented in Table 39. The differences between Fe^{2+} and Fe_T concentrations at any point in time during the tests indicated that a significant amount of the iron had been removed by an oxidation process due to the iron-oxidizing bacteria which might still have been present. The amount of Fe^{2+} removed was at the 100 percent level for 34 of the total 42 hours of the seven 6-hour tests. For the entire duration of the test, at least a 50 percent level of Fe^{2+} removal was attained.

A high level of removal of Fe_T was also demonstrated during these tests. Adsorption is the probable mechanism for the removal of Fe^{3+} ($Fe_T = Fe^{2+} + Fe^{3+}$). The 50 percent removal level for this species of iron was attained for the same total time period as in the removal of Fe^{2+}, 34 of the total 42 hours of the tests. At a flow rate of 30 ml/min, this amount of the bacteria-impregnated carbon could be used to treat 61,200 ml of water of this quality and attain 50 percent removal of the iron. Stated differently, one pound of this carbon could treat over 9 gallons of water of this quality based on these tests. For this process to be practical, the removal of iron from actual mine waters must clearly be more effective than demonstrated in these tests with synthetic coal mine waters.

TABLE 38. CONTINUOUS FLOW TESTS WITH BACTERIA-INOCULATED CARBON

Time,	"Standard" Test - No Bacteria Experiment No. 443-5		Bacteria Added to Water Experiment No. 443-7		Bacteria Added to Carbon Experiment No. 443-31	
min	Fe^{2+}, mg/l	Fe_T, mg/l	Fe^{2+}, mg/l	Fe_T, mg/l	Fe^{2+}, mg/l	Fe_T, mg/l
0	235	240	188	560	224	260
5	28	39	182	184	37	336
10	28	29	208	266	19	223
15	38	39	220	292	20	214
30	133	150	278	525	12	202
45	145	162	180	550	10	211
60	156	173	170	500	24	214
90	170	175	163	540	12	213
120	176	182	150	185	42	216
150	182	190	138	575	70	204
180	190‡	196‡	120	565	83	194
210	-	-	145*	600*	100	200
240	-	-	-	-	110	195
270	-	-	-	-	106	191
300	-	-	-	-	114	211
330	-	-	-	-	114	191
360	-	-	-	-	108	183

‡ Test discontinued after 180 min.
* Test discontinued after 210 min.

TABLE 39. LONG TERM EFFECTS OF THIOBACILLUS FERROOXIDANS

Time, min	Experiment No. 440-99 mg/1		Experiment No. 451-2 mg/1		Experiment No. 451-3 mg/1		Experiment No. 451-4 mg/1		Experiment No. 451-5 mg/1		Experiment No. 451-6 mg/1		Experiment No. 451-7 mg/1	
	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T
0	250	266	263	286	250	295	253	266	260	279	263	269	250	266
5	0	13	0	42	0	75	0	42	0	62	0	88	0	58
10	0	29	0	52	0	78	0	45	0	71	0	107	13	71
15	0	23	0	55	0	78	0	49	0	94	0	117	13	103
30	0	16	0	71	0	75	0	49	0	101	0	120	16	117
45	0	13	0	91	0	84	0	55	0	104	0	156	26	130
60	0	13	0	97	0	94	0	75	0	104	0	159	19	136
90	0	23	0	114	0	117	0	94	0	127	-	-	-	-
120	0	36	0	120	0	156	0	107	0	127	0	175	23	143
150	0	58	0	133	0	149	0	117	0	127	-	-	-	-
180	0	81	0	143	0	153	0	123	0	130	3	188	26	195
210	0	89	0	143	0	159	0	131	0	140	-	-	-	-
240	0	107	0	143	0	169	0	136	0	149	32	208	42	221
270	0	123	0	143	0	166	0	143	0	153	-	-	-	-
300	0	127	0	156	0	169	0	156	0	149	78	201	104	224
330	0	120	0	159	0	169	0	153	0	156	-	-	-	-
360	6	127	0	156	0	172	3	161	0	159	88	208	127	234

Effect of Long Aeration Periods Prior to Testing

While the differences between the effectiveness of iron removal using this bacteria-inoculated carbon and carbon which had not been inoculated with bacteria were attributed to the bacteria, there may have been other reasons for differences in effectiveness. Before using the column containing the carbon and bacteria, the column was aerated continually and the ferrous sulfate solution "changed" approximately every other day (on the weekend, the solution was changed on the third day). The continual aeration of the carbon for the expressed purpose of maintaining bacterial activity might also have resulted in changing the nature of the carbon. Lamb and Elder (10) reported (a) that charcoal when prepared fresh and dry showed a positive test for a peroxide (b) that no further test for peroxide was seen after extraction of the charcoal with acid and (c) that the sample of charcoal once extracted could again be made to give an equally positive test for peroxide by shaking the residual charcoal with more water and air. The effect of air (oxygen) on charcoal was also recognized by others (29-34).

To demonstrate the effect of a long aeration period, a comparison was made between a bacteria-inoculated carbon and a carbon without bacteria. Each carbon had been aerated continually for at least one month under a solution of ferrous sulfate which was "changed" every other day. The first series of continuous flow tests according to the general procedure was conducted with synthetic coal mine water. The results are presented in Table 40 and were similar whether bacteria were present or not.

The second series of continuous flow tests was conducted with an actual coal mine water. The results of these tests are presented in Table 41 and again are similar whether bacteria were present or not.

In both series of tests, aerating the carbons for long periods of time prior to using them in the tests resulted in very effective removal of Fe^{2+} accompanied by less effective removal of Fe_T. An additional continuous flow test was conducted with activated alumina which was aerated continually for 18 days prior to the test and a solution of standard synthetic coal mine water added as in past tests. The results of this test with actual coal mine water showed virtually no removal of Fe^{2+} and only a slight removal of Fe_T, indicating little or no oxidation with the activated alumina and possibly a slight amount of adsorption or filtration of precipitated Fe^{3+} compounds by the alumina.

From these tests of relatively short duration, the long aeration of the carbon prior to use resulted in effective removal of Fe^{2+} and less effective removal of Fe_T, which is most desirable for this process since the iron would be oxidized but not adsorbed by the activated carbon. This favorable removal of iron occurred whether bacteria were present or not.

TABLE 40. COMPARISON OF THE EFFECT OF LONG AERATION PERIODS AND BACTERIA VERSUS NO BACTERIA ON REMOVAL OF IRON FROM SYNTHETIC COAL MINE WATER

	No Bacteria Added Experiment No. 444-95					Bacteria Added Experiment No. 444-96				
		Fe^{2+}		Fe_T			Fe^{2+}		Fe_T	
Time, min	pH	mg/l	Percent Removed	mg/l	Percent Removed	pH	mg/l	Percent Removed	mg/l	Percent Removed
0	3.1	240	--	260	--	3.0	253	--	266	--
30	2.8	0	100	0	100	2.3	0	100	52	80
60	3.7	0	100	0	100	2.3	0	100	68	74
120	2.5	0	100	49	81	2.2	0	100	81	70
180	2.4	0	100	78	70	2.2	0	100	101	62
240	2.4	0	100	94	64	2.2	0	100	104	61
300	2.4	0	100	110	58	2.2	0	100	110	59
360	2.4	0	100	123	53	2.2	0	100	123	54

TABLE 41. COMPARISON OF THE EFFECT OF LONG AERATION PERIODS AND BACTERIA VERSUS NO BACTERIA ON REMOVAL OF IRON FROM ACTUAL COAL MINE WATER

	No Bacteria Experiment No. 444-97					Bacteria Experiment No. 444-98				
		Fe^{2+}		Fe_T			Fe^{2+}		Fe_T	
Time, min	pH	mg/l	Percent Removed	mg/l	Percent Removed	pH	mg/l	Percent Removed	mg/l	Percent Removed
0	3.1	127	--	159	--	3.1	127	--	159	--
30	2.8	0	100	42	74	2.7	0	100	62	61
60	2.7	0	100	45	72	2.7	0	100	45	72
120	2.7	0	100	62	61	2.7	0	100	62	61
180	2.8	0	100	62	61	2.8	0	100	62	61
240	2.7	0	100	62	61	2.7	0	100	62	61
300	2.7	0	100	65	59	2.7	0	100	65	59
360	2.7	0	100	68	57	2.7	0	100	68	57

Tests with Bacteria-inoculated Coal

Tests were conducted using bacteria alone, carbon alone, and combinations of bacteria and carbon. To examine the effect of the combination of bacteria and a solid surface other than activated carbon, nine tests were conducted according to the general procedure but with coal which had been inoculated with Thiobacillus ferrooxidans 15 days prior to the first test with this material. The results of these tests seemed to indicate effective removal of iron with the use of material other than activated carbon. In spite of the fact, though, that the pH of the effluent from the column remained low throughout these tests, iron could be seen precipitating onto the coal in increasing amounts as these tests progressed. This precipitation, by itself, may have been responsible for the apparently effective removal of iron. Since these tests were conducted near the end of the project, time was not available for further study in this area.

Statistical Design III

To further explore the matter of the need for bacteria or long aeration of the carbon prior to use, a third set of factorial experiments was designed to cover the effects of water flow rate, amount of carbon, bacteria versus no bacteria, and aeration rate on continuous removal of iron from an actual coal mine water. Each series consisted of 16 tests. In eight of the tests, separate samples of carbon were inoculated with Thiobacillus ferrooxidans at least 18 days prior to the test, the carbon columns aerated continually, and a ferrous sulfate solution added periodically as in past tests. The other eight tests were conducted with carbons which had not been inoculated with bacteria. As in past experiments, only the second of two successive tests with each column was evaluated. The data representing the 16 tests are presented in Table 42.

For ease of interpretation, again the four separate variables are identified, with the high and low level of each variable being represented by + and - signs respectively. The procedure for evaluating this factorial experiment was identical to that described previously in the Statistical Design I and II experiments. The data in Table 42 were again employed in the calculation of both main effects and variable interactions for the seven responses for this test using the codified design and calculation matrix previously presented in Table 11 and the procedure previously outlined. The main effects are listed in Table 43.

From the data in Table 43, the most significant variable affecting Fe^{2+} and Fe$_T$ removal was Variable 1, the flow rate of the water through the column. The negative sign for that main effect simply meant that iron was removed more effectively at the lower flow rate of raw water (20 ml/min in this experiment). The importance of this variable remained apparent throughout the duration of each test as indicated by the relatively large value for that main effect (See Table 43). In the first few hours of each test this effect of flow rate was greater on the removal of

TABLE 42. RESULTS OF STATISTICAL DESIGN III EXPERIMENT ON VARIABLES AFFECTING IRON REMOVAL

	Variables*											
	1	2	3	4	After 30 min		After 60 min		After 120 min		After 180 min	
Test	Water Flow Rate	Amount of Carbon	Bacteria	Aeration Rate	Fe^{2+} % Removed	Fe_T % Removed	Fe^{2+} % Removed	Fe_T % Removed	Fe^{2+} % Removed	Fe_T % Removed	Fe^{2+} % Removed	Fe_T % Removed
1	-	-	-	-	100	100	100	100	100	100	100	100
2	+	-	-	-	59	52	36	44	34	37	32	35
3	-	+	-	-	100	100	100	100	100	100	100	100
4	+	+	-	-	100	100	100	97	91	89	79	79
5	-	-	+	-	100	89	100	82	100	60	100	48
6	+	-	+	-	75	32	71	22	62	14	42	9
7	-	+	+	-	100	100	100	100	100	100	100	100
8	+	+	+	-	100	87	100	73	100	54	100	45
9	-	-	-	+	100	100	100	100	100	100	100	100
10	+	-	-	+	83	71	79	54	70	40	66	40
11	-	+	-	+	100	100	100	100	100	100	100	100
12	+	+	-	+	100	99	95	91	74	79	67	76
13	-	-	+	+	100	81	100	66	100	56	100	44
14	+	-	+	+	69	41	63	25	51	22	46	25
15	-	+	+	+	100	100	100	100	100	100	100	100
16	+	+	+	+	100	88	100	44	100	39	100	31

* Variable Identification

	Levels	
Variable	+	-
Water Flow Rate	80 ml/min	20 ml/min
Amount of Carbon	1,000 g	500 g
Bacteria	YES	NO
Aeration Rate	500 ml/min	50 ml/min

TABLE 42. RESULTS OF STATISTICAL DESIGN III EXPERIMENT ON VARIABLES AFFECTING IRON REMOVAL (continued)

	Variables*									
	1	2	3	4	After 240 min		After 300 min		After 360 min	
Test	Water Flow Rate	Amount of Carbon	Bacteria	Aeration Rate	Fe^{2+} % Removed	Fe_T % Removed	Fe^{2+} % Removed	Fe_T % Removed	Fe^{2+} % Removed	Fe_T % Removed
1	-	-	-	-	100	100	100	100	100	100
2	+	-	-	-	40	24	41	25	44	29
3	-	+	-	-	100	100	100	100	100	100
4	+	+	-	-	65	67	26	58	20	57
5	-	-	+	-	100	48	92	41	84	33
6	+	-	+	-	39	7	37	8	37	8
7	-	+	+	-	100	100	100	100	100	100
8	+	+	+	-	100	45	100	42	100	40
9	-	-	-	+	100	100	100	100	100	100
10	+	-	-	+	64	38	64	37	68	34
11	-	+	-	+	100	100	100	100	100	100
12	+	+	-	+	59	69	26	58	20	57
13	-	-	+	+	100	43	99	42	72	39
14	+	-	+	+	43	10	38	22	43	24
15	-	+	+	+	100	100	100	100	100	100
16	+	+	+	+	100	29	90	29	76	29

* Variable Identification

	Levels	
Variable	+	-
Water Flow Rate	80 ml/min	20 ml/min
Amount of Carbon	1,000 g	500 g
Bacteria	YES	NO
Aeration Rate	500 ml/min	50 ml/min

TABLE 43. MAIN EFFECTS BASED ON DATA FROM CONTINUOUS FLOW TESTS

	Fe^{2+} Removed, percent		Fe_T Removed, percent		Fe^{2+} Removed, percent		Fe_T Removed, percent	
	Variable	Main Effects	Variable	Main Effects	Variable	Main Effects	Variable	Main Effects
	After 30 Minutes				After 60 Minutes			
Single Variable:	1	-14.25	2	26.00	1	-19.50	1	-37.25
	2	14.25	1	-25.00	2	18.25	2	26.50
	4	2.25	3	-13.00	4	3.75	3	-21.75
	3	.25	4	2.50	3	3.00	4	-4.75
	After 120 Minutes				After 180 Minutes			
Single Variable:	1	-27.25	1	-42.75	1	-33.50	1	-44.00
	2	18.50	2	29.00	2	20.00	2	28.75
	3	5.50	3	-25.00	3	5.50	3	-28.50
	4	1.00	4	-2.25	4	3.25	4	0.00
	After 240 Minutes				After 300 Minutes			
Single Variable:	1	-36.25	1	-50.25	1	-46.13	1	-50.50
	2	17.25	2	30.00	3	12.38	2	26.50
	3	6.75	3	-27.00	2	8.88	3	-24.25
	4	2.75	4	-.25	4	2.63	4	1.75
	After 360 Minutes							
Single Variable:	1	-43.50	1	-49.25				
	2	8.50	2	27.00				
	3	7.50	3	-25.50				
	4	-.75	4	2.00				

Designation of Variables:
1 = Water Flow Rate
2 = Amount of Carbon
3 = Bacteria
4 = Aeration Rate

Fe_T than it was on the removal of Fe^{2+}; but by the end of the 6-hour tests, the effect was equally pronounced on both Fe_T and Fe^{2+}.

Of lesser importance was the effect of Variable 2, the amount of carbon used. The value of the effect of this variable on Fe_T was approximately one-half the value of Variable 1. This variable had a practically insignificant effect on removal of Fe^{2+}. The positive value for this effect meant that greater removal was attained with the greater amount of carbon used (1,000 g in this experiment).

Similarly, Variable 3 affected the removal of Fe^{2+} and Fe_T to a degree similar to that of Variable 2. The negative sign for the effect on Fe_T indicated that greater removal of iron was demonstrated when bacteria were not added to the carbons prior to use. The positive sign for the effect of this variable on Fe^{2+} indicated that the bacteria aided in the removal of Fe^{2+}. The effect on Fe^{2+}, though, was much less than the effect on Fe_T as indicated by the absolute magnitude of this variable. These results are consistent with the probabilities that (a) the presence of iron-oxidizing bacteria or the use of long aeration periods of the carbon prior to use should aid in the oxidation of Fe^{2+}, and (b) adsorption of iron onto the surface of the activated carbon as measured by Fe_T would be inhibited by the presence of bacteria blocking the active carbon sites for adsorption.

Variable 4, aeration rate, at the levels of this experiment, had no affect on removal of iron as demonstrated by the relatively small value for this effect from Table 43.

The values for many two-variable interactions were as great as those for Variables 2 and 3, but these relatively high values did not persist for single two-variable interactions throughout the duration of the tests.

Effect of Water Flow Rate

In the first of this series, standard synthetic coal mine water was used. The results of continuous flow tests conducted according to the general procedure but with water flows of 30, 100, 150, 200, 300, and 600 ml/min are presented in Table 44. From the data in Table 44, the amount of iron removed decreased for both Fe^{2+} and Fe_T with increasing flow rate.

In the second of this series, an actual coal mine water was used. Water from a tributary of Little Plum Creek, sampling point No. 2 (See Table 31), was chosen. The results of these tests at water flow rates of 30, 60, and 120 ml/min are presented in Table 45. The flow rate of 30 ml/min is included in the general procedure. Only the results of the second of two successive tests with water at the specified flow rate are included in Table 45, for reasons previously discussed. From these data, little direct relationship could be found between water flow rate and removal of Fe^{2+}. For this series of tests, more effective Fe^{2+} removal was seen at the higher flow rate, 60 ml/min, than at a lower flow rate, 30 ml/min.

TABLE 44. EFFECT OF FLOW RATE ON REMOVAL OF IRON FROM SYNTHETIC COAL MINE WATER

	30 ml/min			100 ml/min			150 ml/min			200 ml/min			300 ml/min			600 ml/min		
	Experiment No. 444-53			Experiment No. 444-54			Experiment No. 444-54			Experiment No. 444-53			Experiment No. 444-49			Experiment No. 444-49		
Time, min	pH	Fe^{2+} mg/l	Fe_T mg/l	pH	Fe^{2+} mg/l	Fe_T mg/l	pH	Fe^{2+} mg/l	Fe_T mg/l	pH	Fe^{2+} mg/l	Fe_T mg/l	pH	Fe^{2+} mg/l	Fe_T mg/l	pH	Fe^{2+} mg/l	Fe_T mg/l
0	3.0	253	266	3.0	253	266	3.0	253	266	3.0	253	266	3.0	263	286	3.0	263	286
5	2.9	166	211	2.8	159	208	2.9	101	137	3.0	94	101	3.9	192	208	3.1	218	240
10	2.9	162	201	2.9	159	208	2.9	101	140	3.3	130	169	3.9	201	244	3.1	208	240
15	3.0	156	162	2.9	153	201	2.9	110	159	3.3	156	205	3.7	237	253	3.1	208	237
30	2.9	133	179	2.8	153	208	3.0	114	159	3.1	166	205	3.6	244	256	3.0	208	250
45	2.9	133	166	2.8	159	205	2.9	149	201	3.0	175	201	3.3	250	260	3.0	204	247
60	2.9	130	159	2.8	199	208	2.8	156	224	2.9	179	224	3.2	231	266	3.0	201	240
90	2.8	143	172	2.8	159	205	2.8	159	218	2.9	175	208	3.1	224	240	3.0	207	240

TABLE 45. EFFECT OF WATER FLOW RATE ON REMOVAL OF IRON FROM TRIBUTARY OF LITTLE PLUM CREEK. SAMPLING POINT NO. 2.

	Flow Rate = 30 ml/min					Flow Rate = 60 ml/min					Flow Rate = 120 ml/min				
	Experiment No. 451-26					Experiment No. 451-29					Experiment No. 451-32				
		Fe^{2+}		Fe_T			Fe^{2+}		Fe_T			Fe^{2+}		Fe_T	
Time, min	pH	mg/l	Percent removed	mg/l	Percent removed	pH	mg/l	Percent removed	mg/l	Percent removed	pH	mg/l	Percent removed	mg/l	Percent removed
0	3.0	114	--	282	--	3.3	172	--	227	--	3.2	182	--	256	--
30	4.6	13	89	42	85	4.6	29	83	71	69	4.4	156	14	185	28
60	4.3	32	72	91	68	4.5	71	59	104	54	4.4	159	13	182	29
120	4.3	91	20	120	57	4.4	94	45	120	47	4.1	156	14	205	20
180	4.3	99	13	134	52	4.3	97	44	117	48	3.7	188	0	224	13
240	4.2	101	11	133	53	4.2	101	41	114	50	3.2	175	4	221	14
300	4.1	101	11	133	53	4.1	104	40	117	48	3.2	169	7	198	23
360	4.1	101	11	129	54	3.9	136	21	146	36	3.1	166	9	192	25

However, the least effective Fe^{2+} removal was found at the highest flow rate of this series, at 120 ml/min.

Also from these data, the expected decrease in Fe_T removal with increasing flow rate can be seen.

It must be pointed out here that with this particular actual coal mine water sample, the rate of removal of either Fe^{2+} or Fe_T was not good at any flow rate, nor as good as was obtained in earlier tests with synthetic coal mine water. The reasons for this have not yet been clearly defined, but the low dissolved oxygen content of this water as sampled has already been discussed.

In the last of this series, the combined activated carbons from the Statistical Design III experiment, a total of 6500 g of carbon, were placed in a 52 in. x 5 in. column. The carbon was aerated continually for about 3 weeks with a ferrous sulfate solution added periodically as in past tests. This carbon was then used in tests with actual coal mine water with water flow rates of 20, 200, 400, 800, and 1600 ml/min. Water from a tributary of Little Plum Creek, sampling point No. 1, was seclected because of the high concentration of iron in this water. The results of these tests are presented in Table 46. Generally speaking, the results show a decrease in iron removal with increasing flow rate. These data will be employed more fully in the following section.

TABLE 46. EFFECT OF FLOW RATE ON REMOVAL OF IRON FROM TRIBUTARY OF LITTLE PLUM CREEK. SAMPLING POINT NO. 1

Time, min	pH	Fe^{2+} mg/l	Fe^{2+} Percent Removed	Fe_T mg/l	Fe_T Percent Removed
Flow Rate 20 ml/min Experiment No. 451-75					
0	2.8	279	--	419	--
60	2.7	0	100	13	97
120	2.7	0	100	13	97
180	2.7	0	100	13	97
240	2.8	0	100	13	97
300	2.8	0	100	16	96
360	2.8	0	100	16	96
Flow Rate 200 ml/min Experiment No. 451-78					
0	2.9	282	--	422	--
60	2.7	45	84	156	63
120	2.7	55	80	182	57
180	2.7	84	70	244	42
240	2.6	104	63	286	32
300	2.6	117	59	325	23
360	2.6	136	52	334	21
Flow Rate 400 ml/min Experiment No. 451-77					
0	2.8	292	--	435	--
60	2.6	49	83	237	46
120	2.6	75	74	341	22
180	2.6	127	57	370	15
240	2.7	172	41	373	14
300	2.7	179	39	373	14
360	2.7	201	31	373	14
Flow Rate 800 ml/min Experiment No. 451-76					
0	2.8	318	--	448	--
60	2.5	0	100	295	34
120	2.5	0	100	354	21
180	2.5	62	81	383	15
240	2.6	133	58	390	13
300	2.7	188	41	373	17
360	2.7	205	36	386	14
Flow Rate 1600 ml/min Experiment No. 451-79					
0	2.8	286	--	468	--
60	2.6	172	40	419	10
120	2.7	201	30	419	10
180	2.7	218	24	419	10
240	2.7	231	19	416	11
300	2.7	231	19	419	10
360	2.7	234	18	419	10

SECTION VI

SUMMARY EVALUATION OF IRON REMOVAL WITH ACTIVATED CARBON

Based on the results of the laboratory studies which were presented in the preceding section, the following is a summary evaluation of the process for removal of iron from acid mine drainage with activated carbon.

Aeration with No Carbon Present

To demonstrate the effect of aerating acid mine drainage containing ferrous iron at low pH, the following experiment was performed. A 19 in. x 3 in. glass column was packed with approximately 800 g of 3/8 in.-diameter glass beads and a continuous flow test conducted according to the general procedure with actual coal mine water containing Fe^{2+}. The results are presented in Table 47. From these data, aeration of the acid mine drainage at low pH in the absence of activated carbon had no effect whatsoever on removal of iron.

Aeration with Activated Carbon Present

From the results of the laboratory studies described in the preceding section, aeration of acid mine drainage in the presence of activated carbon resulted in removal of iron from the water at a rate which was affected greatly by the experimental conditions. In addition, it was also demonstrated that the relative rates of removal of Fe^{2+} and Fe^{3+} were influenced by the experimental conditions. The removal of Fe^{2+} proceeded by a combination of oxidation and adsorption. The removal of Fe^{3+} proceeded by adsorption. The most desirable mechanism for removal of iron from acid mine drainage is removal of only Fe^{2+} by oxidation. This oxidation would result in conversion of Fe^{2+} to Fe^{3+} which would then remain in solution. The activated carbon would not eventually be rendered inactive and would not need to be replaced with fresh activated carbon. Removal solely by an oxidation process, however, has not been experienced on this project.

In the last series of tests on this project, the experimetnal conditions selected were those found from all previous tests to result in most effective removal of iron. The results of these tests with 6500 g of carbon and actual coal mine water flow rates of 20, 200, 400, 800, and 1600 ml/min were listed in Table 46. For the purposes of this evaluation, the data from Table 46 were plotted in Figure 17 and consideration given to the time during which 50 percent of the Fe^{2+} was removed in these tests. The 50 percent level of iron removal was somewhat arbitrarily chosen as an attainable, or, at least, a measurable goal.

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TABLE 47. EFFECT OF AERATION ON REMOVAL OF IRON. NO CARBON

Time, min	pH	Fe^{2+} mg/l	Fe^{2+} Percent Removed	Fe_T mg/l	Fe_T Percent Removed
0	2.7	350	0	535	0
5	2.7	350	0	535	0
10	2.6	350	0	535	0
15	2.6	350	0	535	0
30	2.6	350	0	535	0
60	2.6	350	0	535	0
120	2.6	350	0	535	0
180	2.6	350	0	535	0
240	2.6	350	0	535	0
300	2.6	350	0	535	0
360	2.6	350	0	535	0

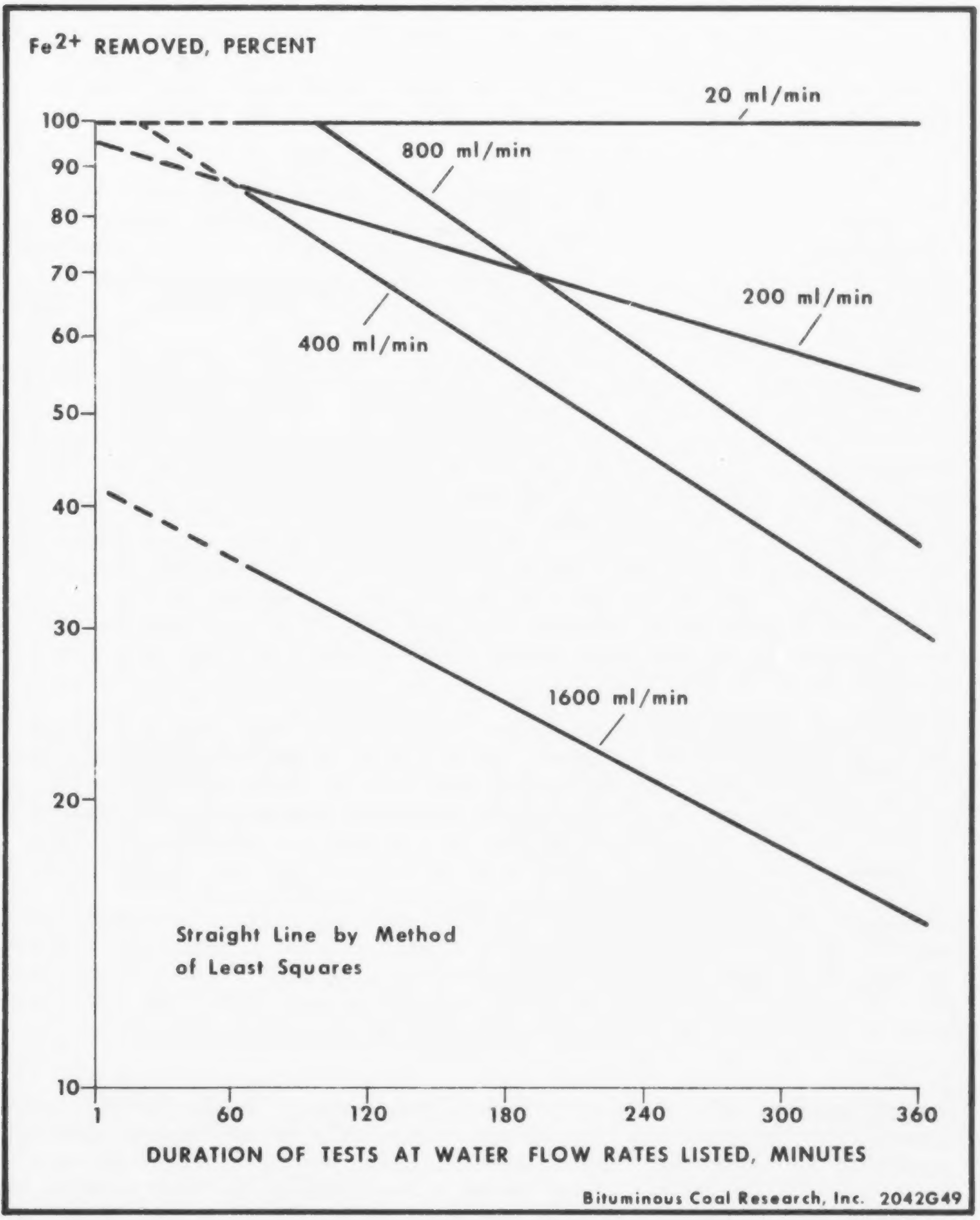

Figure 17. Effect of Water Flow Rate on Removal of Fe^{2+}

As can be seen from Figure 17, at a flow rate of 20 ml/min, 100 percent of the Fe^{2+} was removed for the duration of the test. This flow represents only a few gallons of water treated per day, a rate too small to be treated practically. At that low water flow rate, no indication was given of the deterioration of the carbon with time during this short test. Conversely, from Figure 17, at the highest water flow rate, 1600 ml/min, the rate of removal was very low and the 50 percent level of removal was never attained.

For this evaluation, consideration was given first to the tests at a water flow rate of 200 ml/min. A 50 percent level of Fe^{2+} removal was attained for slightly better than 6 hours in this test. At 200 ml/min, this corresponds to a rate of approximately 19 gallons treated to the 50 percent Fe^{2+} removal stage in a 6-hour period using 6500 g of carbon before the carbon was spent. At about 22 cents per pound for the particular carbon used, this represents 0.75 lb of carbon necessary to treat one gallon of water, or a materials cost of $165 per thousand gallons of water treated.

Similarly, at a flow rate of 800 ml/min, 6500 g of carbon was used to treat approximately 51 gallons of water in a 4-hour period to the 50 percent level of Fe^{2+} removal. At the same price per pound of carbon, this corresponds to a materials cost of approximately $62 per thousand gallons of water treated. (From Figure 17, the apparently more effective removal of Fe^{2+} at 800 ml/min as compared to 400 ml/min can be attributed simply to the fact that the 800 ml/min test was conducted prior to the 400 ml/min test and the carbon had not yet been rendered quite so inactive.)

Since total costs for treatment of acid mine drainage including chemicals, labor, capital cost, etc., are reported to be from about 10 cents to slightly more than $1.00 per thousand gallons of water treated, it is clear that cost of treatment with activated carbon based on these studies would be prohibitive to the use of this process for acid mine drainage.

It is felt that further studies in this area might result in some increases in the rate of removal of iron with activated carbon by changes in the configuration of the reactor or by using many columns in series. Increases in the rate of removal of a sufficiently large magnitude to make this process practical are not anticipated.

The key to a practical process seems to be in finding a method of easily removing the adsorbed iron from the carbon. These studies have shown that this adsorbed iron clings tenaciously to the carbon thereby rendering it inactive. "Regeneration" of the spent carbon should not be considered in the classical sense; i.e., reactivation and removal of adsorbed contaminants by a heat treatment step. Neither heat treatment nor an acid wash, as found from these studies, will remove adsorbed iron from the activated carbon.

Another possibility is that a replacement for the activated carbon might be found which might react similarly and yet not adsorb iron so strongly or else be sufficiently inexpensive that once having adsorbed the iron, the spent material might be discarded.

A third possibility is that some level of iron removal less than 50 percent might be tolerated in a continuous treatment system, such as in a limestone neutralization system. The effectiveness of this combination on an activated carbon-limestone treatment process can only be ascertained by actually testing such a system.

In summary, a method has been found for removing iron from acid mine drainage containing ferrous iron by using activated carbon. The method, though technically feasible, is prohibitively expensive.

SECTION VII

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* * *

A significant objective of this project was to investigate practical means of abating mine drainage pollution. Such research projects, intended to assist in the prevention of water pollution by industry, are required by Section 6b of the Water Pollution Control Act, as amended. This project of EPA was conducted under the direction of the Pollution Control Analysis Section, Ernst P. Hall, Chief, Dr. James M. Shackelford, Project Manager, and Eugene Harris, Project Officer.

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SECTION VIII

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16. Abstract

Laboratory studies were conducted with activated carbon as a catalyst for oxidation of ferrous iron in coal mine water. Batch tests and continuous flow tests were conducted to delineate the process variables influencing the catalytic oxidation and to determine the number and types of coal mine water to which this process may be successfully applied.

The following variables influence the removal of iron with activated carbon: (a) amount and particle size of the carbon; (b) pH, flow rate, concentration of iron, temperature, and total ionic strength of the water; and (c) aeration rate. Adsorption as well as oxidation are the mechanisms involved in iron removal by this process.

An evaluation of this process indicated technical feasibility which would permit acid mine drainage neutralization using an inexpensive reagent, such as limestone. The major disadvantage is the cost of the activated carbons since they are rendered inactive after relatively short use by apparently irreversible adsorption of iron. This cost appears to be sufficiently high to prohibit the use of this process for treating coal mine drainage. (Ford--Bituminous Coal Research, Inc.)

17a. Descriptors
*Acid Mine Water, *Waste Water Treatment, *Activated Carbon, Iron Compounds, Oxidation, Adsorption, Ferrobacillus

17b. Identifiers
*Iron Removal, Oxidation Catalyst

17c. COWRR Field & Group 05D

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